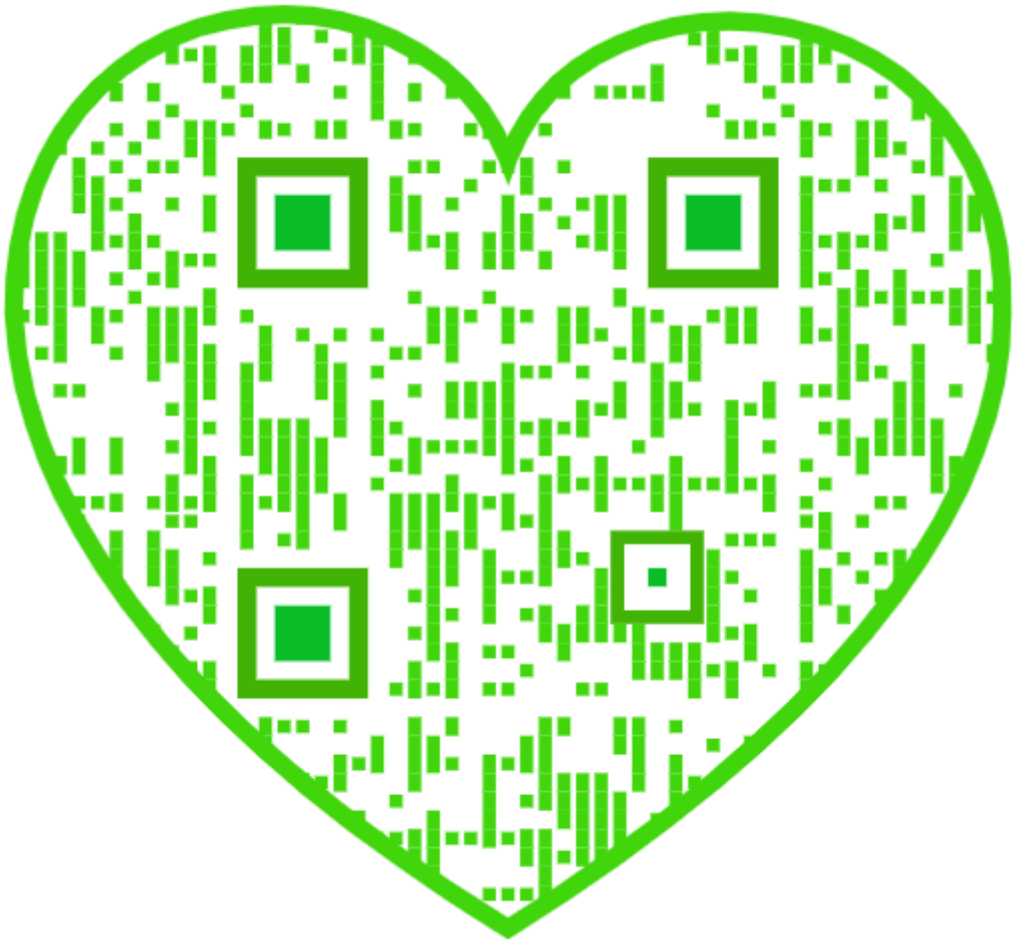
SEWAGE · ANALYSIS



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AND

EFFLUENTS FROM SEWAGE

BY

J. ALFRED WANKLYN

AND

WILLIAM JOHN COOPER

INCLUDING ALSO A CHAPTER ON

UTILISATION AND PURIFICATION

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PREFACE

By J. ALFRED WANKLYN

This book is one of a series of treatises on special applications of chemical analysis, the first of these treatises, which is now in its tenth edition, having been published so long ago as the month of May in the year 1868. The first of these books, the "Water-Analysis," although specially concerned with drinking-water and the recognition of the chemical differences between clean and unclean water, was not complete without some reference to sewage, which is a pre-eminently unclean, and a very common variety of water. Accordingly, so long ago as the year 1874, on the appearance of the third edition, there was a chapter on urine and sewage; and the ammonia method of sewage-analysis, described in that edition and all later editions of "Water-Analysis," has since come into general use.

The acceptance of a sound method of analysis, which is perhaps the only redeeming feature in the official or semi-official analyses of sewages and sewage-effluents, and the only circumstance which saves them from utter futility, is deprived of much of its value and its power for good by reason of confusion of systems of numerical statement.

As the author of "Albuminoid Ammonia," the writer

has from the very first—now more than thirty years ago —always expressed the readings of albuminoid ammonia in terms of parts per million (milligrammes per litre) of water, or sewage, or sewage-effluents.

The scale, parts per million or milligrammes per litre, was proposed by William Allen Miller in the year 1865, in his excellent paper on the analysis of water; and in the year 1867, when the ammonia method was originated, the results of that method were expressed on that scale, and no departure from that scale has ever been sanctioned by the originator of the method. When a chemist discovers a new metal, it is customary for that chemist to name the metal, and confusion would arise if other chemists were to give other names to the metal.

The ammonia process of water-analysis has come into use abroad, and out of this country no instance of the expression of results in any way but that sanctioned by the author has ever come under his notice. In England, two other scales, viz., parts per 100,000 and grains per gallon, have been, most improperly, employed by some of those persons who use the ammonia process. No reason—except such reasons as most persons are ashamed to avow—can possibly be given for the failure of certain English chemists to express the results of the ammonia process on the only scale ever sanctioned by the author.

This tampering with analytical results is rapidly assuming the dimensions of a public scandal, inasmuch as public authorities are being misled in consequence of the persistence of some English chemists in so unwarrantable a procedure. An instance of the practical results arising from this tampering has recently come prominently for-

ward. The so-called bacteria beds at Sutton yielded an effluent giving 2.40 milligrammes of albuminoid ammonia per litre. The published figure, however, is 0.170, which is calculated to deceive public authorities, who naturally assume that chemists working the ammonia process would, as a matter of course, adopt the only scale ever sanctioned by the author of the process and the manual in which that process was described. The difference between the two figures is the difference between success and failure. And the originator of albuminoid ammonia warns those persons who employ the ammonia process that the expression of the results in parts per hundred thousand lays the analyst under the suspicion of representing the liquids as being ten times too pure, and the expression of results in grains per gallon makes the liquids seem fourteen times better than the reality.

Official sewage-analyses of the present day, in addition to these records, which are correct in principle but are blurred by an irregular and confusing manner of expression, comprise another kind of record which is fundamentally at fault. The eminent Danish chemist, Forchhammer, first "proposed to employ a solution of potassic permanganate for the determination of the amount of organic matter in water." That occurred so long ago as the year 1850, and —as W. A. Miller told the Chemical Society in his discourse published in the year 1865—Forchhammer's discovery attracted little attention at first, and Forchhammer has never had justice done to his memory.

It was the privilege of the writer to be present on an occasion when Forchhammer gave an account of one of the branches of water-analysis, and he remembers well the

kindly reception which the communication met with from Faraday, the most noble English chemist of this century.

Forchhammer's method is capable of measuring the organic matter in water, and even in that very impure variety of water called sewage, when it is used in a proper manner.

In the year 1878,[1] Forchhammer's dream was accomplished—the proper manner of using the permanganate so as to burn down almost all organic substances to carbonic acid and water was discovered—and "moist combustion" became as real a laboratory operation as Liebig's dry combustion with red-hot oxide of copper, and the famous Liebig's potash bulbs for recording the carbonic acid.

Why certain official chemists in England still persist in the use of the permanganate in a manner in which it is incapable of performing moist combustion cannot be explained. There is no reason except such reasons as most persons are ashamed to avow.

Meanwhile the public consequences of this official perversity are most serious, and we find the Salford effluents giving utterly irreconcilable analytical results. That most careful chemist, Mr. Carter Bell, finds one thing, and the capable chemists of the Mersey and Irwell Joint-Committee arrive at a conclusion which is for all practical purposes in diametrical opposition.[2]

The scandal of this discrepancy lies neither at the door of Mr. Carter Bell nor of the capable chemical workmen

[1] *Vide* Appendix.

[2] *Vide* Mr. Carter Bell's paper in the *Journal of the Society of Chemical Industry*, 31st January 1898, No. 1, vol. xvii. : "On the Oxygen Test for Sewage and Effluents, as carried out in the Laboratory of the Mersey and Irwell Joint-Committee."

who perform the Joint-Committee's work, but at the door of some one else, whom the writer is not called upon to indicate.

In this current year, 1899, the reformation of the analysis of sewage and of the effluents from sewage is as much a public need as reformation of the analysis of ordinary drinking-water was in the year 1867, when albuminoid ammonia was first discovered.

The object of this book is to bring about this reform, and to point the way to the proper disposal of sewage, which is, indeed, a matter of vital importance to the nation, and which is dealt with in detail in Chapter VIII.

In some respects the opportunities enjoyed by my colleague and myself are absolutely unique. For the space of nearly thirty years we have been in the active practice of those branches of our profession which are concerned with sanitation in its various aspects. In the year 1867, on the occasion of the bringing out of the ammonia method of water-analysis, one of us was brought into intimate personal relations with the late Mr. Way, at that time the chemist on the Rivers Pollution Commission; and in the year 1875, as the colleague of Mr. Way, he made the first recorded analysis of sewage in which the amount of complex nitrogenous organic matter was measured by means of albuminoid ammonia, and carried out an inquiry into the condition of the Harrogate sewage farm. In the year 1880 the other of us made analyses of the effluents from the highly successful sewage works of the Native Guano Company in Aylesbury.

At intervals during several years the Croydon sewage farm was under our investigation. The Coventry sewage

works, the Hertford sewage works, the camp at Aldershot, the Salford sewage works, and many other works have furnished materials for our instruction, and have contributed to educate us and prepare us for the task before us. The neighbourhood of our laboratory has, of late years, furnished us with instructive instances illustrative of essential points in the treatment of sewages.

In some degree the peculiar circumstances under which our work has been carried on—for example, the severance of all relations with the London Chemical Society—has operated to our advantage.

The wave of fad and fallacy at present passing through the Chemical Society has not disturbed us in our laboratory. Bacteria are interesting creatures, and the study of them is an interesting department of zoology and natural history. But bacteria are subject to gravitation and to general physical and chemical action; neither is the burning of the kitchen-fire nor the action of the steam-engine a manifestation of bacterial action. And equally true is it that much of the actual change in dilute solutions and semi-solutions of miscellaneous organic matter is quite independent of bacterial action. The oxidation of organic matter in suspension or in solution in aqueous liquids is capable of being brought about by some organic materials, which are certainly not alive, and even by materials which are of a purely mineral character.

In the book which is now published we have treated the subject broadly, and have availed ourselves of materials from many sources.

In our introductory chapter we deal with sewage from a synthetical point of view. We know the materials

which go to make it, and these materials must exist in the sewage except in so far as interior changes have modified them.

In Chapter I. we deal with that most general and elementary physical property, viz., the density or specific gravity as compared with pure water. This depends upon that which is dissolved or suspended in the liquid, and (subject to some limitations) might be deduced from the composition of the sewage; and that view of the subject is further developed in the Appendix to the book.

Chapter IV. is devoted to carbonic acid, which is a very important (and almost entirely neglected) constituent of sewage. By the fermentation of urea, carbonic acid is produced in relatively large quantities, and by the oxidation of other substances in sewage it is also produced, so that the carbonic acid becomes predominant.

Chapter VI. is on the moist combustion process, which we hope will replace the, at the present time, much used abortive employment of the permanganate; and this chapter includes an indictment of the fashionable method of procedure. The exposure of error is often a thankless task, but it is a necessary prelude to the establishment of truth. In the Appendix, under the heading "The Chemistry of Manganese," our views on this subject are enforced and supported by a great variety of evidence of many kinds.

In many respects, but not in all, our views are in accordance with those of Mr. Carter Bell, whose paper—giving his experiences as the responsible chemist in charge of the large and important sewage works of the Salford Corporation—we publish in his own words and almost without

abridgment. Our readers will be interested in Mr. Carter Bell's latest experiences, which, among the rest, include observations on the application of electricity to the purification of sewage.

J. ALFRED WANKLYN.

LABORATORY, NEW MALDEN,
SURREY, *February* 1899.

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SEWAGE-ANALYSIS

INTRODUCTION.

During the present century now drawing to its close, there has been a great alteration in the manner of disposing of our visible excreta. The old-fashioned privy, with its attendant horrors, has given place to the modern water-closet, and we rid ourselves and our dwellings of our visible excreta by resorting to a convenient system of water-carriage. The penalty which we have to pay for this convenient method of disposal is the production of sewage, which is the mixture of refuse and water which passes into the sewers.

In order rightly to understand the subject of sewage, it will be useful to call to mind certain broad biological facts in the routine of daily existence. Thus it is instructive to note that the visible excreta from the human body, viz., the discharge from the bladder and the discharge from the alimentary canal, are comparatively small, the great excretion being the invisible excretion issuing from the lungs.

In the space of twenty-four hours the lungs of a full-grown man discharge more than 800 grammes of carbonic acid, whilst the combined dried-up urine and fæces during the twenty-four hours amounts to only about 90 grammes.

About nine-tenths of the daily excretion takes place by

way of the lungs, and is disposed of involuntarily by aërial carriage, and only the remaining tenth is left for us to dispose of by artificial means, and to manage or mismanage as the case may be. This remaining tenth of the daily excreta affords scope for the sewage-system, and, entering the sewers, gives rise to the sewage.

We next proceed to give a description of each of the two important excretions of which this remaining tenth is composed; and we begin with the urine, which, in many respects, is the more important of the two.

In the year 1874, in the third edition of the "Water-Analysis," one of us wrote as follows:—

"The urine, as is well known, is an excretion the composition and quantity of which are subject to great variation, according to the condition of the animal economy.

"Thus, among a number of urinary analyses recorded in my own notebook, there is an instance of urine containing 4.52 grammes of solids in 100 c. c., and an instance of urine containing 1.40 gramme of solids in 100 c. c.

"The latter specimen of urine had been passed shortly after drinking a quantity of beer, and illustrates a very well-known physiological fact, viz., that after drinking considerable quantities of liquid the urine becomes watery.

"In like manner, the quantity of urine produced in the twenty-four hours is subject to variation, depending to a great extent on the needs of the animal system.

"But although specimens of urine may vary much, and although the quantities of urine excreted under particular circumstances may be very different, still the urine passed by any hundred persons taken at random must be pretty constant both in quality and in quantity.

"According to Parkes, the average quantity of urine passed by a healthy man in twenty-four hours is about 1500 c. c., containing about 4.07 grammes of solids in every 100 c. c. Of these 4.07 grammes 2.21 grammes consist of urea. Next in quantity comes the common salt; and thus urine consists chiefly of urea and common salt. In addition to the urea, urine contains some other organic substances in smaller quantities, viz., extractive matter, colouring matter, uric acid, hippuric acid, and creatinine. Besides common salt, there are likewise other mineral ingredients, such as sulphates and phosphates."

The following statement of the composition of fresh unfermented urine of average quality may be put forward as substantially correct, and sufficient for our present purpose.

In one litre :—

	Grammes.
Urea	20
Other organic matter	7
Ash or mineral matter	13
	40

The composition of the 13 grammes of mineral matter is as follows :—

	Grammes.
Chlorine, Cl	4.3
Sulphuric acid, SO_3	1.6
Phosphoric acid, P_2O_5	1.6
Sodium, Na	4.0
Potassium, K	0.8
Calcium, Ca	0.18
Magnesium, Mg	0.14
	12.62

The deficiency 0.38 is sufficiently accounted for by the

circumstance that, whilst the basic portion of the mineral matter is expressed by metals, the acid portion is partly expressed by a halogen and partly by anhydrous sulphuric and anhydrous phosphoric acid. If the SO_3 be replaced by "sulphuric halogen," SO_4, the figure 1.6 would become 1.92, and in that manner the deficiency would be nearly made up. If the phosphoric acid were also replaced by phosphoric halogen, the total constituents of the ash would then somewhat exceed the 13 grammes.

In giving the foregoing numerical details, we have availed ourselves of a well-known standard authority on the subject, and we have ourselves verified the substantial accuracy of most of that which we are putting forward.

That, for instance, 40 grammes per litre is a fair expression for average urine, is in conformity with our laboratory experience. The urine of one of us, examined at different dates, has furnished the following results:—

In the year	1871	. .	45.2	grammes	per litre.
„	„	. .	38.6	„	„
„	1872	. .	37.4	„	„
„	1898	. .	38.4	„	„

Urine from three other sources examined in our laboratory has given:—

40.3	grammes	per litre.
38.6	„	„
44.0	„	„

In these examples the subject was in good health, and urine presumably normal was dealt with. In two of the examples the urine was passed before breakfast, "twelve hours after taking food or drink" being the note in one instance. The average of the seven examples is 40.35 grammes of

total solids per litre of urine. We have set down the average mineral matter in a litre of urine as 13 grammes. Our own results, taken by themselves, would lead to a slightly higher figure, viz., to 14 or 15 grammes.

Of the various constituents of the mineral matter, the chlorine and the sulphuric acid have been recently determined in our laboratory, the chlorine having been determined by weighing the chloride of silver obtained from 50 c. c. of urine, and the sulphuric acid by weighing the sulphate of baryta from 50 c. c. of urine. Our figure for chlorine, viz., 4.3, is a little below that given by Parkes, viz., 4.66.

Our figure for sulphuric acid is a little higher than Parkes's. Our figure for phosphoric acid was obtained from work in our laboratory many years ago; it is smaller than Parkes's. The figure given in "Watts's Dictionary"* as sodium in 1500 c. c. of average urine, viz., 11.09, is evidently erroneous. That would be at the rate of 7.39 grammes per litre of average urine, and such a figure is not possible: it would involve an amount of ash far too high to be consistent with the actual ash found by direct experiment.

Urine is peculiarly liable to fermentation, and sometimes

* In Michael Foster's article on Urine in "Watts's Dictionary" there is a curious error, which is, no doubt, partly typographical. The total solids in the day's urine passed by an average man, weighing 66 kilos., are stated as being 61.14 grammes. But, on adding up the weights of the various constituents of the 61.14 grammes, we have a total amounting to 72.048 grammes. This excess (which is very nearly 11 grammes) is partly made up by the excessive figure for sodium, and partly by the excessive figure for "pigment and extractives." Apparently the extractives include some chloride of sodium, which, therefore, is counted twice.

even the fermentation commences before the urine leaves the bladder. The principal chemical change brought about by the fermentation is the conversion of the urea into carbonate of ammonia by reaction upon water, thus :—

$$\underset{\text{Urea.}}{CH_4N_2O} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbonate of Ammonia.}}{(NH_4)_2OCO_2}.$$

In the year 1880 we had an opportunity of making observations on a large scale, having had at our disposal the undiluted urine of the North Camp at Aldershot.

We found the specific gravity 1017.4 at 60° Fahrenheit (water at exactly the same temperature being taken as 1000.0). The urine was powerfully alkaline, and 50 c. c. saturated 18 c. c. of normal acid. It contained 4.40 grammes of fixed organic matter and 10.6 grammes of mineral matter in one litre.

Its composition was, therefore, as follows :—

	Grammes per Litre.
Carbonate of ammonia, $(NH_4)_2OCO_2$.	17.28
Fixed organic matter	4.40
Mineral matter	10.60
	32.28

The sample operated upon was taken from a large bulk, from at least 3000 litres, the composition of which is represented by the analysis.

On another occasion, in dealing with a large volume of urine, we observed even a higher degree of alkalinity, 50 c. c. requiring 20.5 c. c. of normal acid in order to neutralise it. The carbonate of ammonia, therefore, amounted to 19.68 grammes per litre.

Unless special precautions be taken to prevent the urinary

fermentation, the mere storage of a large volume of urine brings about the complete, or almost complete, destruction of the urea. Indeed, the proneness to this kind of fermentation has been recognised for the last fifty years. In Lehmann's famous treatise on "Physiological Chemistry," translated by the Cavendish Society nearly fifty years ago, there is the following passage (vol. ii. p. 410):—

"Normal urine passes more or less rapidly into the alkaline fermentation when the temperature exceeds 20° C.; this change is effected very readily when the urine has been kept in unclean vessels, and almost at once when mixed with urine which has become alkaline, even when the quantity added is so small as hardly to saturate the free acid of the fresh urine."

It is quite intelligible, and quite in accordance with the recognised chemical history of urine, that the accumulated urine of the camp should be charged with carbonate of ammonia, and devoid, or nearly devoid, of urea. A comparison of this fermented urine with fresh normal liquid is instructive, and brings out several points of interest.

The amount of mineral matter in this fermented urine is rather less than in normal urine. At first sight this would seem to suggest a little dilution with water; but there is another explanation. In becoming alkaline the liquid would deposit phosphates of lime and magnesia, which accounts for a slight fall in the proportion of mineral matter.

A very interesting point in the urinary fermentation, as distinguished from the well-known vinous fermentation of saccharine liquids, is that the urinary fermentation does not sensibly lower the specific gravity of the liquid. This

fact came out very clearly at Aldershot. We found the specific gravity of the first great bulk of fermented urine to be 1017.4, and the specific gravity of the second great bulk nearly the same, viz., 1017.5.

The explanation of the non-lowering of the specific gravity is quite obvious: the carbonate of ammonia resulting from the destruction of the urea raises the specific gravity on entering into aqueous solution.

Strikingly in contrast with all this is the alcoholic fermentation of sugar, wherein lowering of specific gravity forms so prominent a feature.

The question has often been asked—In the fermentation of urea is the conversion of the urea into carbonate of ammonia quite complete?

Our observations at Aldershot lead us to reply that apparently about three-quarters of the urea undergoes conversion into carbonate of ammonia, and one-quarter is otherwise disposed of.

Our experiments bring out a most important fact—the urinary fermentation involves in its sphere of action more substances than the urea originally present. Before fermentation the total organic solids in the liquid amount to about 27 grammes per litre; after fermentation they have fallen to 4.4 grammes per litre, an amount which is unquestionably less than the non-ureal portion of organic matter in normal urine.

Passing on to the description of the other important excretion, viz., the fæces, we will again make reference to Lehmann's "Physiological Chemistry," translated, under the auspices of the Cavendish Society, by Dr. Day. In vol. ii. page 141 we read: "Important as is the investi-

gation of this subject for physiologists, and especially for physicians, our investigations regarding it are as yet few and of doubtful accuracy. The analysis of the solid excrements is, however, attended with so many difficulties, and is so disgusting a task, that we find it exciting the complaints even of a Berzelius." And a little farther on we read: "An adult in a state of health, living on a mixed diet, usually discharges in the course of twenty-four hours from 120 to 180 grammes of semi-solid brown masses." Farther on it is stated that "these brown masses contain about 25 per cent. of solid constituents, so that from 30 to 45 grammes of solid dry matter are daily carried off in the intestinal evacuations of a healthy man living on a mixed diet."

Since that was written, it would appear that, notwithstanding the repulsive nature of the work, a chemist of the name of Wehsarg has mustered courage to make an elaborate investigation of the matter, and his results are to be found among additions and notes to vol. ii. Wehsarg's conclusion from his work is, that "*the absolute quantity of solid matters discharged in the twenty-four hours averages* 30 *grammes.*"

In the course of his investigations Wehsarg has put on record the very wide variations which actually occur in the total quantity of this discharge during periods of twenty-four hours. In seventeen periods of twenty-four hours each, the highest figure was 306, and the lowest 67.2 grammes of wet fæces. The mean of the seventeen observations was 131 grammes. He remarks that "this irregularity did not seem in any way connected with an excess of undigested matter," and he laid down "as a general rule, that when the food

passes rapidly through the intestine, the daily quantity of the fæces is larger than when it is retained for a longer time in the intestine. In proportion to the rapidity with which the stools follow one another, there is a smaller relative but a larger absolute amount of solid matters. There is no definite relation between the amount of fæces and the bodily weight; the quantity of the fæces seems rather to be connected with the digestive power of the individual."

In Watts's Dictionary, under the heading "Excrements," there is a slightly different version of these results. "From the observations of Wehsarg it appears that a full-grown healthy man discharges on an average in twenty-four hours 131 grammes of fæces containing 26.7 per cent. of solid matter (dried at 120° C.), therefore 35 *grammes of solid matter in twenty-four hours.*"

The slight discrepancy arises no doubt from the manner of arriving at the average of 26.7 per cent. of solid matter. Probably that average was arrived at by taking the mean of all his observations, whilst that the "absolute quantity of solid matters discharged in the twenty-four hours averages 30 grammes" is evidently a direct experimental result. No doubt Wehsarg dried up separately the fæces of each day, and weighed the dry residue of each day. The seventeen dry residues would then be added together, and the total would be divided by 17 so as to obtain the daily average.

For our present purpose it is of little consequence whether the more accurate figure be 30 or 35 grammes.

Only a small proportion of this excretion is immediately soluble in water; only about one-fifth, or about 6 grammes, passes into solution in water. This is quite intelligible, inasmuch as the fæces are the terminal portion of the in-

testinal contents—the remnant after everything absorbable has been absorbed and passed into the general circulation. Fæces are necessarily most miscellaneous in composition. They contain the insoluble substances taken in with the food, and sometimes food which has not undergone digestion. There are also biliary products and substances coming from the walls of the intestinal canal. A by no means inconsiderable proportion of the fæces is non-nitrogenous; there are always some fatty substances, and there is cellulose and woody fibre—all of which are non-nitrogenous. The total nitrogen in the average day's fæces is 2.5 grammes. The mineral matter in fæces is very small, the 30 or 35 grammes of the dry daily excreta containing only about one-twentieth of mineral matter.

Having thus described the two great excretions which form our visible excreta, we are now in a position to commence the description of sewage. The actual amount of the dried-up urine and fæces has been set down as about 90 grammes per individual of the population per diem. In forming sewage this becomes largely diluted with water. In many English towns the quantity of water poured into the sewers considerably exceeds 30 gallons for each individual. Putting this at 150 litres per individual of the population (about 33 gallons), which is by no means excessive, we arrive at the result that the dilution is such that 150 litres of sewage contains 90 grammes of excretal products. Each litre of sewage would thus appear to be charged with 0.6 gramme of material of excretal origin. Of this 0.4 is urinary and 0.2 is fæcal.

We have mentioned that one-half of the urinary solids is urea, yielding by immediate fermentation ammonia and

carbonic acid, which are inorganic substances. After making allowance for the mineral matters contained in the two excretions, we are landed at the conclusion that *typical* sewage contains 0.300 gramme of excretal organic matter per litre.

Of this 300 milligrammes it would appear that only a small portion is at first in perfect solution, and the following statement may be useful in order to picture the composition of sewage in its first stage.

In one litre:—

	Milligrammes.
Excretal organic matter in suspension . .	= 220
„ „ in perfect solution	= 80
„ „ Total . .	= 300

This statement assumes that beyond the inevitable and immediate urinary fermentation, *no* other destruction takes place during the dilution of the day's excreta with the day's water-supply.

It takes no account of the soap, which of course is not an excretal substance, but which adds to the organic contents of sewage.

Of the consumption of soap the remark may be made, that the soap used for personal washing and the washing of clothes goes into the sewers; and that some, but by no means all, of the soap used in other ways for domestic purposes goes into the sewer. We put down the quantity of soap which contributes to the sewage as between 5 and 10 grammes of dry soap per individual per diem. That quantity of soap would raise the organic matter in the day's sewage to the extent of from 30 to 60 milligrammes in the litre of sewage; and inasmuch as there is lime in

most water-supplies, the soap would contribute to the insoluble or suspended organic matter more than to the soluble organic matter in the day's sewage. A noteworthy effect of the soap on the sewage is the contribution of alkali to the sewage, and that favours the setting up of fermentation, and the bringing about of those changes which are involved in the production of sewage.

And in this place the remark may be made, that the water-closet system, with its characteristic production of sewage, may be well carried out or ill carried out. Well carried out, it makes for the health of the community; ill carried out, it is highly insanitary.

The essential conditions of a properly ordered water-closet system are that the supply of water should be abundant, and that there should be no lodgment either in the water-closet or in the sewers, and that the sewage should always be flowing through the sewers.

We have shown that in typical sewage (*i.e.* sewage wherein the day's excreta are mixed with 150 litres of water per individual of the population) there might be 300 milligrammes of organic matter per litre, assuming no chemical changes beyond those involved in the ureal fermentation.

The result of chemical examinations of sewage collected at the outfall of the sewer is, that sometimes more than half of this original organic matter must have disappeared during the passage of the current of sewage along the sewer. There is unquestionably oxidation in the sewers. Most water-supplies contain nitrates, and some waters contain much nitrates. Sewage formed out of water rich in nitrates is of necessity considerably modified by the oxygen

which the organic matter derives from the nitrates, and, in extreme cases, as much as 50 milligrammes of oxygen proceed from the nitrates in a litre of water. All water-supplies contain some atmospheric air in solution, and from that source oxygen is also provided for the oxidation of the organic matter. When there is an abundance of water, much of the original organic matter passes into the inorganic state—into the ultimate inorganic products carbonic acid and water, during the progress of the sewage through the sewers.

The objects aimed at by the chemical investigation of sewage and sewage effluents are manifold.

First, it is quite possible, from the analysis of the sewage at the outfall, to form a fairly correct opinion as to whether or not the supply of water is sufficiently abundant; and if an examination of the sewage be coupled with an examination of the water-supply, a very fair estimate of the number of gallons per head of the population may generally be arrived at.

Secondly, examinations of the sewage effluents, taken at different stages from the sewage works after the sewage has left the sewers, are designed to disclose the degree of approximation to the character of ordinary stream-water arrived at by the sewage-effluents.

The course of analysis about to be described in the following chapters has been laid down with the object of enabling answers to be given to such questions as those which we have just outlined.

The selection of 150 litres of water per head of the population as the standard diluent of the day's excreta is well warranted by the statistics of water-supply to English and

Scotch towns. In a paper read at a meeting of the Social Science Association by an eminent sanitary engineer, Mr. Baldwin Latham, C.E., in Glasgow in the year 1874, the following statistics were put forward.

In twenty towns the average volume of water per head of the population is given in this table.

Names of Water-Closet Towns.	Quantity of Water per Head. Gallons.
Alnwick and Canongate	30
Barnet	30
Croydon	56
Liverpool	26
London	29
Penzance	25
Plymouth	40
Uxbridge	20
Warwick	30
Watford	30
Names of Middenstead Towns.	
Atherton	40
Ayr	38
Bradford	26
Bacup	33
Glasgow	50
Lincoln	30
Malton	40
Ormskirk	40
Perth	30
York	30
20	673
Average	33.65

If a calculation be made, it will be found that 150 litres of water equals 33.07 gallons, which quite bears out our estimate.

It is quite true that, in some towns, the drains form one

system and the sewers another system; but, as Mr. Baldwin Latham remarked in the paper from which we have quoted, the water from both systems requires purification, and nothing is gained by keeping the two liquids separate. Both ought ultimately to reach the sewage-works.

In the famous investigation of the sewage of Rugby in the years 1861, 1862, and 1863, the average amount of sewage per head of the population was about 33 gallons a day; and the average amount of total residue left on evaporating to dryness was 1251 milligrammes per litre; and the total amount of ammonia obtained from a litre had a daily average of 92.7 milligrammes. In this famous investigation no pains were spared to ensure that the numerical results should be *true averages*. The two quantities just given were the mean of the analysis of 93 samples of Rugby sewage collected between April 1861 and October 1863; and each one of the 93 samples was itself an average sample of several days' sewage. The work was carried out in the laboratory of Mr. Way, who was one of the members of the Royal Sewage Commission. The total organic matter in Rugby sewage was likewise measured as loss on ignition. The mean result of the analysis of the 93 samples of the sewage was found to be 393 milligrammes per litre.

At the time when this work was carried out, the only method known to chemists for measuring the amount of organic matter in water or in sewage (which is an especially dirty water) was by means of the loss on ignition. That method is now, in the year 1899, seldom resorted to. When there is very little organic matter, and more particularly when the organic matter is accompanied by many times its weight of mineral matter, the ignition method is quite un-

trustworthy; but, in the instance of raw sewage, where there is much organic matter, and where the accompanying mineral matter is not overwhelmingly preponderating, the loss on ignition is by no means utterly untrustworthy as a measure of the organic matter. This figure, 393, is probably slightly in excess of the truth, and requires a little correction for the water of hydration of the sulphate of lime in the residue before ignition. That correction having been made, the result is approximately true, and it accords with the amount of organic matter arrived at *synthetically:* that is to say, deduced from the materials which are known to pass into the sewers, as we have already explained. The fact that in sewage we find more *organic matter* in the insoluble part of the sewage than in the soluble part of the sewage is likewise well brought out. And tabulating the results of the famous investigation of the Rugby sewage, we have the composition of typical sewage as follows:—

	Milligrammes per Litre.
Mineral matter partly in suspension and partly in solution	859
Organic matter in suspension . . .	269
Organic matter in solution	123
Total	1251

And there is the 92.7 milligrammes of ammonia, which would be mainly in the state of carbonate, equal to 267 milligrammes of carbonates. (*Vide* Paper on the Composition, &c., of Town Sewage, by Lawes and Gilbert, *Journal of the Chemical Society* for the year 1866.)

CHAPTER I.

THE SPECIFIC GRAVITY OF SEWAGE AND SEWAGE-EFFLUENTS.

In the later editions of the treatise on Water-Analysis attention has been drawn to the differences of specific gravity presented by different varieties of drinking-water, and it has been shown that there is utility in making such measurements. Sewage and sewage-effluents are still more open to this kind of investigation.

Inasmuch as the fermentation of urine involves little or no lowering of the specific gravity of the liquid, it follows that sewage must be sensibly higher in specific gravity than the water-supply of the district from which the sewage is derived.

Typical sewage, as we have already mentioned, consists of the day's visible excreta mixed with 150 litres of water per individual of the population, and the day's urine averages 1.5 litre. We may, therefore, regard the dilution of the urine to be a hundred times, and knowing the specific gravity of fermented urine, we are in a position to calculate the influence of the urine upon the specific gravity of the sewage. Our investigation of the urine of the North Camp at Aldershot furnished the number 1017.4 as the specific gravity of large volumes of the fermented urine. In typical sewage made with such urine, the influence of the urine upon the specific gravity of the original water-supply would be to cause a rise of 0.174.

When the original water-supply is soft and little charged with foreign matter, as is the case in some of our northern towns, the original gravity of the water-supply is sometimes as low as 1000.05. When such water produces typical sewage, the rise in gravity due to the urinous part of the sewage brings the gravity up to 1000.224. In the instance of harder waters—London water, for instance—the original water-supply has sometimes a gravity of 1000.30. Typical sewage derived from such water should exhibit a rise of gravity due to urinous constituents bringing the gravity up to 1000.474. The rise in gravity due to fæcal products and to soap and other matters we should set down as about 0.10.

On these principles the specific gravity of the typical sewage in the water-closet town, with the soft water-supply of specific gravity 1000.05, is calculated as being 1000.324; and the specific gravity of the typical sewage in the town with a water-supply of specific gravity 1000.30 is calculated as 1000.574.

In order to be of any value, the measurements of specific gravity have to be very accurate, and some degree of care is indispensable. In particular, it is absolutely essential that the sample of sewage or sewage-effluent should be at exactly the same temperature as the distilled water with which it is compared; or else, if there be any difference of temperature at all, that difference must be small, and must be measured and recorded, and afterwards allowed for. With ordinary care, when the following directions are followed, there will be no difficulty in distinguishing between a specific gravity of 1000.05 and a specific gravity of 1000.07.

A special kind of specific gravity bottle has been designed by one of us for this kind of work. It is represented in the

drawing. The peculiarity is the stopper, which is made to contain a minute reservoir sufficient to hold the liquid which is driven out of the bottle when the contents are slightly warmed by the heat of the hand, which touches the bottle during the operation of wiping with a cloth in order to remove moisture before placing the bottle on the pan of the balance.

Such bottles have been manufactured by Messrs. Baird & Tatlock, 14 Cross Street, Hatton Garden, London, E.C.

The details of the taking of a specific gravity are the following:—

First of all, the sewage, presumably at the temperature of the laboratory, is poured into the clean sp. gr. bottle until there is an overflow of liquid. Then the stopper is carefully inserted, care being taken that no particles of grit prevent the stopper from going home in a satisfactory manner. The next step is to place the filled bottle in an open vessel containing cold water from the tap in the laboratory. The water should reach up to the neck of the bottle, but not above the neck. In this water a thermometer with wide divisions is placed; the water in the bath is stirred up from time to time, and the temperature noted. After the lapse of thirty or forty minutes the temperature is read to one-tenth of a degree Centigrade; and then the superfluous liquid in the stopper is mopped out with little rolls of twisted filter-paper, and—that having been accomplished—the bottle may be taken out of its bath and handled and wiped dry, and finally it has to be weighed.

For comparison with the sewage, distilled water is taken and dealt with just in the same manner as the sewage.

The weight of the bottle-full of distilled water is to be

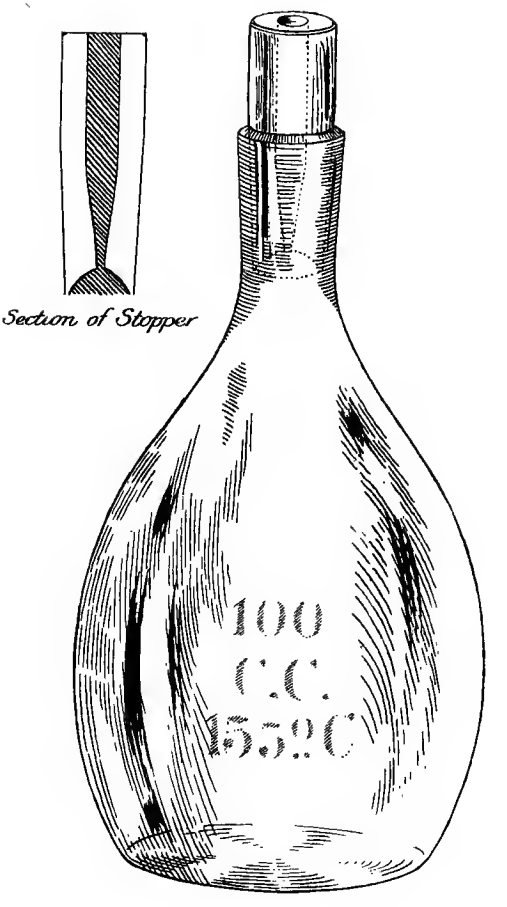

FIG. 1.

subtracted from the weight of the bottle-full of sewage; and the difference, multiplied by 10, gives the figure by which a litre of sewage exceeds in weight a litre of distilled water. Here is an example in illustration:—

	Grammes.	Deg. Cent.
Weight of bottle-full of sewage-effluent =	100.025	at 9.1
„ „ distilled water =	99.930	„ 9.3
	.095	

Therefore specific gravity of the sewage-effluent = 1000.95.

If the correction for the slight difference in temperature (viz. 0.2°) be made, the specific gravity becomes 1000.94.

The correction for temperature should, as far as possible, be avoided by taking measures to have the same temperature in the case of the sewage as in the case of the distilled water. However, in order to deal with cases where there are appreciable differences of temperature, we provide this table:—

Increase in Weight of the 100 c. c. of Distilled Water when the Temperature falls 1° Cent.

Between	20°	and	19°	. . .	17.2	milligrammes.
„	19°	„	18°	. . .	16.0	„
„	18°	„	17°	. . .	15.0	„
„	17°	„	16°	. . .	13.8	„
„	16°	„	15°	. . .	12.6	„
„	15°	„	14°	. . .	11.4	„
„	14°	„	13°	. . .	10.2	„
„	13°	„	12°	. . .	8.8	„
„	12°	„	11°	. . .	7.6	„
„	11°	„	10°	. . .	6.6	„
„	10°	„	9°	. . .	5.0	„
„	9°	„	8°	. . .	3.6	„
„	8°	„	7°	. . .	2.4	„
„	7°	„	6°	. . .	0.8	„
„	6°	„	5°	. . .	—0.4	„
„	5°	„	4°	. . .	—1.8	„

The reason of the minus value during the fall through the two last degrees is explained in the chapter on Specific Gravity in the Water-Analysis.

The manner of using the table is exemplified thus :—

Assuming that 15° Cent. were the temperature of the sewage, and 14° Cent. the temperature of the distilled water, we should correct the weight of the distilled water by subtracting 10.2 milligrammes from the weight of the water; and having done that, we should have placed ourselves in a position to make a correct comparison of the weights of the sewage and the distilled water.

If we take the opposite case, where the temperature of the water is higher than the temperature of the sewage, then we have to make an addition to the weight of the distilled water in order to correct for temperature.

We give the following examples of specific gravities of waters and sewages :—

	Specific Gravity.
Distilled water	1000.00
Sheffield water	1000.05
Rain water	1000.08
Lambeth Water Company . . .	1000.28
Edinburgh Water Supply . . .	1000.16
New Malden sewage—19th Dec. 1898 .	1001.17
„ „ 23rd Dec. 1898 .	1001.30
„ „ 10th Feb. 1899 .	1001.10
New Malden sewage-effluent . . .	1000.95
Salford „ . . .	1000.55
A Lancashire „ . . .	1002.00

In many cases the specific gravity of the sewage is much higher than can be accounted for by the mere admixture of the excretions with the water supply. Additional mineral

matter, generally sulphates, has in these cases found its way into the sewage.

In the Appendix, on page 178, the influence of mineral salts on the specific gravity of solutions is dealt with, and there is a rule for deducing the specific gravity of a mixed solution from the composition of the mixture.

CHAPTER II.

CHLORINE.

THE importance of making a measurement of the amount of chlorine existing in sewage and sewage-effluents arises from the fact that chlorine, in the shape of common salt, occurs in comparatively large proportion in the urine.

One litre of urine, as we have already set forth, contains on an average 4·3 grammes of chlorine.

In typical sewage (wherein one volume of urine has been diluted with water so as to become one hundred volumes) there would be 43 milligrammes of chlorine if the diluting water were absolutely pure.

If the diluting water were from Loch Katrine—where the chlorine is very small, only about 5 milligrammes per litre—then typical sewage should contain 48 milligrammes of chlorine per litre. In London, with its water-supply of about 20 milligrammes of chlorine per litre, the typical sewage should get up to 63 milligrammes. Given the chlorine in the water-supply, required the chlorine in typical sewage produced by that water-supply—is an easy arithmetical problem admitting of very easy solution.

Equally obvious is the answer to the question—Given the chlorine in the water, and given the chlorine in the sewage produced by that water, required the degree of departure

from typical sewage. The following is a case in point found in our laboratory records :—

Chlorine in water-supply, 23 milligrammes per litre.
Chlorine in the sewage, 81 milligrammes per litre.

$$81 - 23 = 58\,;\ \frac{58}{43} = 1.35.$$

The conclusion drawn from these data being that in that instance the sewage was stronger than typical sewage : about $1\frac{1}{3}$ times as strong as typical sewage.

The manner of carrying out the practical work of making the measurements of chlorine in drinking-water was described by one of us in the Water-Analysis. We quote almost verbatim from the text of the third edition, published in 1874, and reprinted in every subsequent edition.

In order to make these measurements of chlorine, we avail ourselves of the well-known reaction of silver-salts on soluble chlorides. When a solution of nitrate of silver is mixed with a solution containing chlorides, the insoluble chloride of silver is produced ; and the quantity of chlorine in a drinking-water, or sewage, or sewage-effluent may be measured by ascertaining how much of a standard solution of nitrate of silver is required in order to precipitate all the chlorine in a certain volume of the liquid.

The standard solution of nitrate of silver is made by dissolving 4.79 grammes of pure nitrate of silver in one litre of distilled water. This solution is of such a strength that 1 cubic centimetre of it is capable of precipitating exactly 1 milligramme of chlorine.

If some of this standard solution be dropped into water containing chlorine, a white precipitate of chloride of silver will continue to form until all the chlorine in the water

has been used up; but, as may readily be seen on making the experiment, there is some difficulty in observing the exact point at which the formation of the precipitate ceases. This difficulty is overcome by using an indicator, which consists of a little chromate of potash. If this be employed, the exact point at which the formation of chloride of silver stops will be marked by the appearance of the deep red chromate of silver.

The principle upon which the indicator depends is, that silver combines with chlorine in preference to chromic acid, and that, accordingly, no red chromate of silver is capable of being formed so long as chlorides are in the water, but that red chromate of silver instantly forms the moment the nitrate of silver is in the slightest excess.

The details of the analysis are as follows:—

100 c. c. of the sample of water is placed in a clean and white porcelain dish. A small quantity of yellow chromate of potash (about 30 milligrammes) is next placed in the water, and stirred up with a glass stirrer until it colours the water distinctly yellow. That having been done, the standard solution of nitrate of silver, which should be contained by a properly graduated pipette, is carefully dropped into the water, which is stirred during this operation. The addition of the silver-solution is continued until the red colour, which forms as the silver-solution touches the water, becomes permanent on stirring. The very earliest point at which the chromate of silver becomes persistent should be read.

Certain precautions ought to be taken in performing these operations. The necessity of the chromate of potash being free from chlorides is almost too obvious to require mention.

Suffice it to add, that there is now no difficulty in meeting with this substance in a state of sufficient purity in commerce. Neither the nitrate of silver nor the sample of water should be acid. If, as occasionally happens, the water be acid, it may be neutralised with pure carbonate of soda; or, indeed, it may be rendered faintly alkaline with advantage.

The reason why acidity has to be avoided is, that chromate of silver is dissolved by acids; and in the determination of chlorine it is our practice, after having noted down the exact point at which the liquid becomes red, to run in about 1 c. c. of the silver-solution in order to make sure that there is no free acid. A very proper precaution is to make a blank trial with distilled water, and also a trial with water containing a known quantity of chlorine before beginning the analysis.

It will often happen that sewage-effluents—and it almost invariably happens that raw sewage—turns the silver-solution black or brown. This arises from the production of sulphuret of silver, or even from the reduction of the silver to the metallic state.

This circumstance occasions a difficulty, and has, no doubt, prevented many persons from resorting to the chlorine measurement in the case of sewages. But the difficulty is very easily surmounted. All that is requisite is to boil the sewage, and allow it to cool before applying the silver-solution; and the practice to follow is this:—

Measure out 100 c. c. of the sewage into a white porcelain dish, then heat to the boiling-point, and boil away about one-tenth of the liquid, then allow to cool, and when nearly cold, apply the silver-solution according to the directions already given.

In order to find out how much chlorine is contained in the litre of the liquid—sewage, sewage-effluent, or drinking-water—the results of the experiment on 100 c. c. are to be multiplied by 10.

Before closing this chapter we think it advisable to remind our readers that, especially in cases where much chlorine is present, the method of producing the chloride of silver by precipitation and subsequent washing, drying, and weighing the chloride of silver, may be resorted to with advantage. When *properly performed*, that method, as all chemists ought to know, is one of the very best in the whole range of analytical chemistry.

The method of operation in the case of sewage is to boil down to about one-tenth a convenient quantity—a litre, for instance—which should be measured. The boiling may be managed in a retort or a flask, or in an evaporating basin. The resulting 100 c. c. or 150 c. c. should then be allowed to cool, and, when cold, it should be slightly acidified with pure nitric acid and filtered through filter-paper. Then a decided excess of solution of nitrate of silver should be added to the filtered liquid, and the resulting curdy precipitate of chloride of silver should be allowed to settle, a considerable addition of nitric acid being made to the liquid after the fact of the nitrate of silver being in excess has been proved. The washing of the chloride of silver should be mainly by decantation, a filter being used to keep back only a very small fraction of the chloride of silver which does not readily settle down. Finally, the main bulk of the chloride of silver is brought into a small porcelain crucible or small thin Berlin porcelain dish, the accompanying water being drained off and passed

through the filter. The chloride of silver in the crucible or dish is dried in the water-bath, and then gently heated till it just begins to fuse at the extreme edge. Ultimately the crucible with the chloride of silver is to be weighed and the weight of the empty crucible subtracted, and in that manner the weight of the main bulk of the chloride of silver is arrived at. The small portion of chloride of silver adherent to the filter is dealt with separately. It is burnt in contact with the paper in a small porcelain crucible, and the resulting silver treated with a drop of nitric acid which dissolves it, and then a few drops of hydrochloric acid are added, and the crucible with its contents gently heated, cooled, and weighed. The weight of the small quantity of chloride of silver obtained in that way is added to the weight of the main bulk, and so the weight of the total amount of chloride of silver from the litre of sewage is arrived at.

In order to calculate the weight of the chlorine contained in this chloride of silver, the rule is to multiply by 0.2473. When the supplementary small lot of chloride of silver is very small, it may be ignited and weighed in the state of metallic silver, and accounted for as metallic silver.

Examples of the amount of chlorine in different waters and sewages :—

	Milligrammes of Chlorine per Litre.
Thames Companies in London	17
New River Company, London	16
Kent Company, London	25
The Rhine at Bonn	9
Harrogate sewage	164
New Malden sewage	72

CHAPTER III.

SULPHATES IN SEWAGE AND SEWAGE-EFFLUENTS.

THE proportion of sulphates in typical sewage is, of necessity, larger than that which is found in the water-supply from which the sewage is derived. Taking 1.6 gramme as the quantity of sulphuric acid in the shape of sulphates in the litre of urine, we calculate the quantity of sulphuric acid as being 16 milligrammes in typical sewage derived by dilution with pure water as the diluent.

The Thames water, as supplied by the West Middlesex Water Company, was found to contain 24.6 milligrammes of sulphuric acid per litre. Such water after furnishing typical sewage would contain 40.6 milligrammes of sulphuric acid in the form of sulphates.

When the Kent Company water forms typical sewage, the figures are :—

Original Kent water, 54 milligrammes of sulphuric acid per litre; and resulting typical sewage, 70 milligrammes of sulphuric acid.

New River water contains very little sulphuric acid, only 13.3 milligrammes per litre, and sewage derived from such water would contain 29.3 milligrammes of sulphuric acid.

Loch Katrine water, according to Wallace, contains 4.7 milligrammes of sulphuric acid per litre, which is one of the lowest yields of sulphuric acid on record in a natural

water. Sewage from such a water would contain 20.7 milligrammes per litre.

As a rule, however, the diluent water contributes at least as much sulphuric acid to the sewage as is contributed by the urine.

It will thus be observed that, although measurements of sulphates are sometimes useful as a guide to the actual degree of dilution which the excreta experience in being converted into a given sewage, these measurements are inferior to the measurements of the chlorine.

Besides the original water-supply and the urine, there is not infrequently another very important source of sulphates in some sewage-effluents. It is not uncommon for crude sulphate of iron and alumina to be added to sewage by way of precipitant.

We regard the measurement of the amount of sulphuric acid in a sewage-effluent as most important in many respects.

The measurement of the amount of sulphuric acid existing in the shape of sulphates in sewage is a very satisfactory analytical operation. A measured quantity of sewage is taken (100 c. c. or 200 c. c. is convenient), and it is acidified with a little pure hydrochloric acid, and if necessary it is filtered; it is heated to boiling, and a moderate excess of solution of chloride of barium is added, and in that way a precipitation of sulphate of baryta is obtained. The liquid is boiled and allowed to cool, and the precipitate is rendered somewhat granular, and is separated by means of a very fine filter-paper and washed, dried, ignited, and weighed.

The amount of sulphate of baryta multiplied by 0.3434 gives the amount of SO_3.

As we have already indicated, it generally happens that

the sewage contains more sulphates than were contained in the water-supply and the excretions from which the sewage was produced. In some instances this excess of sulphates might be explained by the operations of manufacturing industry, and in other instances by the employment of sulphates of iron and alumina as precipitating and deodorising agents. But we find this excess of sulphates even in cases where manufactures are not carried on, and where sulphates of iron and alumina are not employed; and we are driven to the conclusion that there must be some general production or discharge of sulphates in the ordinary course of existence in towns and villages.

CHAPTER IV.

THE CARBONIC ACID IN SEWAGE AND SEWAGE-EFFLUENTS.

In the year 1888, on the occasion of the publication of the seventh edition of the Water-Analysis, one of us called special attention to the carbonic acid existing in natural drinking-waters, and insisted upon the fact that, in many instances, the most abundant single foreign ingredient is the carbonic acid, and that the significance of the carbonic acid is great.

In sewage and sewage-effluents the importance and prominence of the carbonic acid is still more noteworthy, and hitherto the carbonic acid in these liquids has been overlooked almost altogether.

The following record of an experiment recently carried out in our laboratory may be cited in order to illustrate these points.

A sewage-effluent was found to contain 300 milligrammes of carbonic acid in one litre.

The water-supply from which that sewage-effluent proceeded was found to contain 90 milligrammes of carbonic acid in one litre.

It follows, therefore, that 210 milligrammes of carbonic acid was produced by the fermentation and oxidation of the excreta which took part in the formation of that sewage.

For this case we were furnished with the data required for giving an estimate of the degree of concentration of the

sewage. It was not typical sewage, but sewage about $1\frac{1}{3}$ times as concentrated as typical sewage. About 120 milligrammes is the utmost quantity of carbonic acid possible in the shape of the carbonate of ammonia derived from the urea. Most probably the 90 milligrammes of carbonic acid had been derived from the fæcal débris which had undergone oxidation or fermentation.

By recording the carbonic acid in sewage and sewage-effluents we see the possibility of following the changes which take place in the composition of sewages and sewage-effluents during the gradual transformation of the organic substance into its final inorganic forms.

We have devised a method of making these measurements of carbonic acid, and we proceed to describe it.

The principle of the method is the precipitation of the carbonic acid in the form of carbonate of lime, and the subsequent decomposition of the carbonate of lime by means of somewhat dilute hydrochloric acid, and the collection and measurement of the gas in a graduated tube over mercury. The details are as follows :—

A convenient quantity of the sewage or sewage-effluent is measured ; 250 c. c. will be found generally convenient, but sometimes 100 c. c. will be most suitable.

To this we add a moderate excess of clear lime-water, and the mixture is placed in a stoppered bottle and shaken up, and allowed to stand until the precipitate falls to the bottom of the vessel. Then it is partly decanted and partly filtered through a Swedish filter-paper (weight of the paper about 0.50 gramme).[1] Hardly any washing of the precipitate is

[1] By special management the filter-paper may be very much reduced in size and weight.

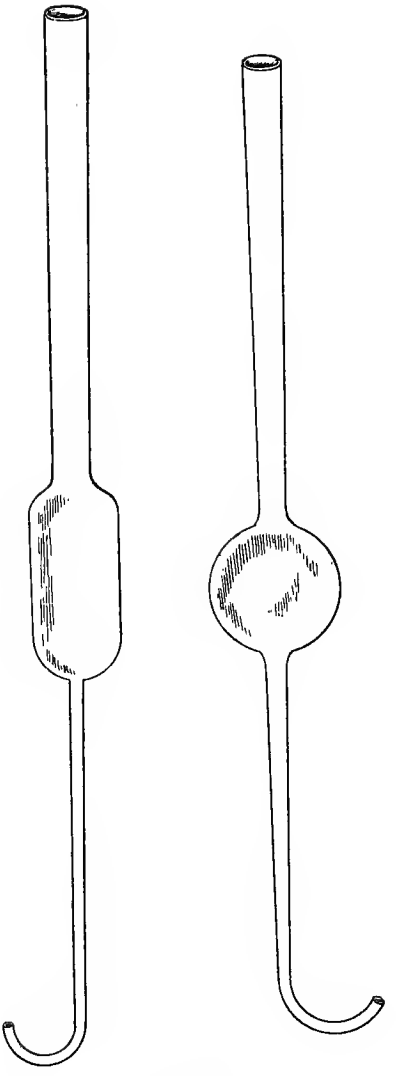

FIG. 2.

required. After allowing the liquid to drain away, the filter, with adherent carbonate of lime, is placed upon several folds of bibulous paper and very gently pressed, and in that manner it is partially dried. Then the filter is carefully folded up (so as to enclose the precipitate), and made into a roll. A Bunsen's absorption tube, capacity from 50 c. c. to 100 c. c., is then filled with mercury and inverted in the mercurial trough. The roll of filter-paper with enclosed carbonate is then introduced into the absorption tube, being passed up through the mercury in the manner familiar to those persons who have had experience in gas-analysis.

It is quite possible to manage this part of the operation without introducing more than 0.2 c. c. of air into the graduated absorption tube. Next, two or three c. c. of moderately dilute hydrochloric acid are passed up into the absorption tube by means of a suitable pipette (*vide* fig. 2).

In contact with the roll of filter-paper charged with the carbonate of lime, this acid liquid will gradually liberate the carbonic acid which will accumulate in the absorption tube. After the lapse of several hours the volume of this gas is read off, together with the height of the mercurial column in the tube; and the temperature is read, and the barometer is also read. The volume of carbonic acid is then reduced by calculation to 0° C. and 760 m. m. pressure.

One cubic centimetre of carbonic acid, at 0° C. and 760 m. m. pressure, weighs 1.9666 milligramme: by making use of this datum, we calculate the weight of the volume of carbonic acid (*vide* Appendix, p. 180).

It is to be noted that, inasmuch as water dissolves almost exactly its own volume of carbonic acid, the small volume of aqueous liquid in the tube may be regarded as if it were

carbonic acid gas, and in that way some minute corrections may be avoided without sensibly impairing the accuracy of the results.

The tension of the aqueous layer may be taken as very nearly the tension of water.

After the necessary readings have been made, the operator may pass up a little strong solution of potash and absorb the carbonic acid, and verify that the residual bubble of air is very small. If so minded, the operator might even measure the air-bubble and correct for it.

As to the filter-paper, it will give no trouble if the plan be adopted of regarding the aqueous layer as equivalent to its own volume of the gas. In that case, even if the paper is above the surface of the aqueous layer, it will not matter, for the bibulous paper charged with water would count as so much of the gas.

The meniscus difficulty, which every one is familiar with, may be dealt with by taking advantage of the circumstance that the reading error due to meniscus is in the opposite direction when the reading is water-level instead of mercury-level.

In order to find the volume of the carbonic acid in the absorption tube, the top of the mercury meniscus is read, and the reading noted down. Then the tube is removed from the mercury trough, emptied out, cleaned, dried, and placed with the open end upwards. Into it is measured, from an accurate burette, so much water as will bring the lowest level of the water meniscus up to the recorded reading of the mercury. The number of c. c. of water thus measured is the true volume of the carbonic acid, corrected for error of meniscus.

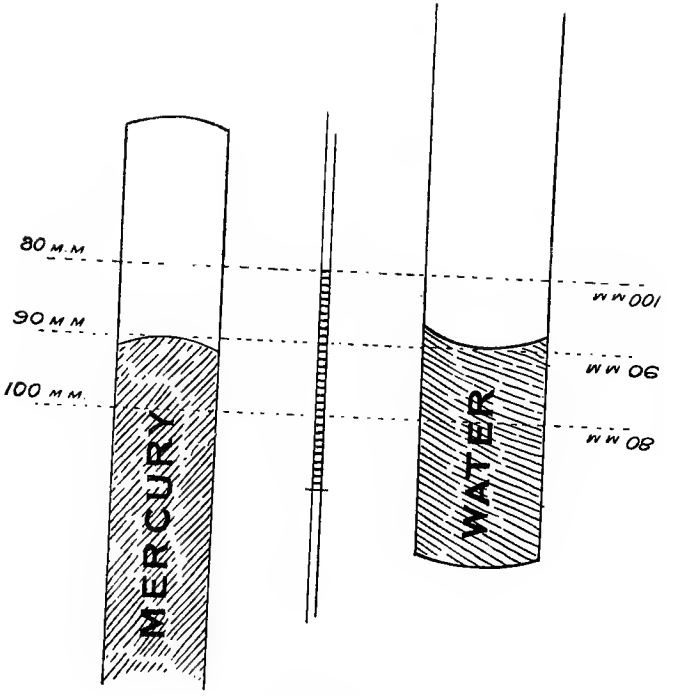

FIG. 3.

This sketch will serve to explain how the compensation comes about.

In our laboratory we make a comparatively small volume of mercury serve for these measurements of carbonic acid; and the well-known Bunsen mercurial trough, which is indispensable when explosions have to be made, is replaced by an arrangement which possesses the advantage of doing away with constant readings of the lower level of the mercury in the trough. These readings are avoided by an automatic overflow of the mercury.

We have to warn any of our readers who may be disposed to resort to these measurements that the evolution of the carbonic acid is slow, and that several hours should be allowed to elapse before making the final reading.

In our hands these measurements of carbonic acid have proved so satisfactory that we are giving the method a wide application to other purposes besides the examination of sewages.

We consider the method which we have been describing to be much better than that which was described in the Water-Analysis. Nevertheless we will repeat the description of the older method for the benefit of those of our readers who may not have the opportunity of manipulating gases.

The carbonic acid in sewage may be measured by taking advantage of the insolubility of carbonate of lime in presence of lime-water. For this purpose lime-water is prepared by taking slaked lime and shaking it up with distilled water, and then allowing to settle, and ultimately decanting the clear supernatant lime-water. One litre of lime-water contains 1.372 gramme of CaO.

In measuring the carbonic acid in the sample of sewage,

it is convenient to take 250 c. c. of the sewage and mix it with 250 c. c. of lime-water in a stoppered vessel. The mixture is allowed to stand until the precipitate of $CaOCO_2$ has settled and the supernatant liquid becomes clear. The liquid is decanted, and the precipitate placed on a filter, slightly washed, burnt in a platinum dish or crucible, and finally weighed. If the resulting carbonate of lime be multiplied by 4, the product will be the carbonate of lime from one litre of sewage. Multiplying by 0.44, the product is expected to be the carbonic acid, in all shapes, in the litre of sewage.

There are, however, several weak points in this method as applied to sewage and sewage-effluents. The first and most obvious defect in the method is that the lime-water precipitates from sewage and sewage-effluents many other things besides carbonate of lime. It carries down any phosphates that may be either in suspension or in solution. It precipitates alumina and magnesia. It forms lime-soaps with any soap which may be in solution. And there are other substances which are precipitated by the lime-water. The examination of the sewage-effluent above cited affords a most instructive example of the danger of trusting to an unexamined lime-precipitate in the instance of sewage or sewage-effluents.

A litre of the sewage-effluent yielded 960 milligrammes of gently ignited lime-precipitate. If that had been pure carbonate of lime, the carbonic acid in the litre of sewage would have been found thus :—

$$960 \times 0.44 = 422.4.$$

And there would be 422.4 milligrammes of carbonic acid in the litre of the sewage-effluent.

By operating upon the effluent in the manner above described, and measuring the carbonic acid gas, it was found that the real amount of carbonic acid was only 300 milligrammes per litre of the sewage-effluent.

Rain-water, and in general the water-supply from a gathering-ground, contains very little carbonic acid, and in such cases practically the whole of the carbonic acid found in the sewage is due to the destruction and oxidation of the organic excreta which make their way into the sewers. In the cases of the water-supply being from rivers or springs, the carbonic acid in the sewage (after a deduction for the carbonic acid belonging to the water-supply), is likewise due to the destruction of organic excreta.

CHAPTER V.

THE AMMONIA-METHOD OF SEWAGE-ANALYSIS—FREE AND ALBUMINOID AMMONIA.

From the very beginning—now thirty-one years ago—the ammonia-method of water-analysis invented by Chapman, Smith, and one of us was employed in the analysis of water heavily laden with sewage, and within the first few years of its existence it was applied by its authors to the analysis of sewage-effluents and sewage itself. Furthermore, within one year of the first inception of the method a most laborious supplementary investigation was undertaken by the authors of the method. In that supplementary investigation, typical nitrogenous substances of the most varied character were subjected to experiment, and the conclusion was arrived at that solutions of complex nitrogenous organic substances of the degree of concentration of sewage are suitable for the application of the ammonia-method.

The general acceptance of the ammonia-method for the analysis of the different kinds of water, from the exquisitely clean on the one hand, down to the very polluted varieties, including sewages themselves, on the other hand, will doubtless be well known to the great majority of our readers.

The method is now so well known that we may abridge our description of it.

The following are the chief requisites demanded for the performance of the analysis :—

1. Nessler reagent.
2. Dilute standard solution of ammonia.
3. Solution of potash and permanganate of potash.
4. Distilled water.
5. Retort and oil-bath.
6. Liebig's condenser.
7. Lamp and retort-holder.
8. Glass cylinders for Nessler test—Nessler glasses.
9. 100 cubic centimetre flask and 250 cubic centimetre flask.
10. Measure for solution of potash and permanganate of potash.
11. Graduated burette.
12. Pipette for Nessler reagent.

Also bottles, a glass funnel, &c.

(1.) The *Nessler Reagent* consists of a solution of iodide of potassium saturated with periodide of mercury, and rendered powerfully alkaline with potash or soda. It is prepared by taking 35 grammes of iodide of potassium and 13 grammes of corrosive sublimate, and about 800 c. c. of water. The materials are then heated to boiling, and stirred up until the salts dissolve. That having been accomplished, a cold saturated solution of corrosive sublimate in water is cautiously added until the red periodide of mercury, which is produced as each drop of the solution falls into the liquid, just begins to be permanent. In this manner we obtain the solution of iodide of potassium saturated with periodide of mercury, and it remains to render it sufficiently alkaline, and to render it

sensitive. This is accomplished by adding 160 grammes of solid caustic potash, or 120 grammes of caustic soda, to the liquid, which is afterwards to be diluted with water, so that the whole volume of the solution may equal one litre. In order to render the Nessler reagent sensitive, it is mixed finally with a little more cold saturated solution of corrosive sublimate, and allowed to settle.

When properly prepared, the Nessler reagent has a slightly yellowish tint. If it be perfectly white, it is sure not to be sensitive, and requires a further addition of solution of corrosive sublimate in order to render it sensitive. Before being employed, it should be tested to ascertain its condition. For this purpose about 2 c. c. of the Nessler reagent are dropped into a very weak solution of ammonia (strength about 0.05 milligramme of HN_3 in 50 c. c. of water), and if it be in proper condition, it will *at once* strike a yellowish-brown tint with the solution.

The stock of Nessler reagent should be kept in a well-stoppered bottle, from which a little is poured out from time to time into a smaller bottle used to contain the Nessler reagent which is about to be used.

(2.) *Dilute Standard Solution of Ammonia.*—It will be found convenient to keep two solutions, a stronger solution and a weaker solution. The stronger solution is made by dissolving 3.15 grammes of chloride of ammonium in one litre of distilled water. (The commercial sal ammoniac, in dry fibrous crystals, answers very well for the purpose.) If the solution be prepared, as has just been described, it will contain one milligramme of ammonia in one cubic centimetre of solution. The weaker solution is prepared by diluting the stronger one with 99 times its volume of

distilled water. The weaker solution, which therefore contains $\frac{1}{100}$ milligramme of ammonia in one cubic centimetre, is generally useful.

(3.) *The Solution of Potash and Permanganate of Potash* is made by dissolving 200 grammes of solid potash and 8 grammes of crystallised permanganate of potash in a litre of water. The solution is boiled for some time, in order to get rid of all traces of ammonia and organic nitrogenous matter; and after about one quarter of the liquid has boiled off, it may be filled up with pure distilled water, so as to bring the solution up to the litre. Each water-analysis requires 50 c. c. of the solution; wherefore each analysis consumes 10 grammes of potash and 0.4 gramme of permanganate.

(4.) *Distilled Water.*—This should be free from all traces of ammonia, and must be tested by the operator.

(5.) *Retort and Oil-Bath.*—Sewages may be operated upon either in a tabulated retort of the ordinary kind, or in a flask-retort.

The retort should hold about a litre of water when it is quite full.

The flask-retort is especially suitable for employment in the oil-bath, and should be much smaller, about 200 c. c.

The oil-bath is conveniently made of copper, and should be adapted to the size of the flask-retort.

(6.) *The Liebig's Condenser.*—A large condenser will be found to be suitable. In our laboratory we use a large copper condenser, 60 centimetres long, and 7 centimetres in diameter; the glass tube which passes through it having a diameter of about 3 centimetres, and a length of about 90 centimetres. As will be perceived, the glass tube of the condenser is wide enough to admit of the beak of the retort

entering it without being drawn out by the blow-pipe. The most convenient packing is a little writing-paper, which is wrapped round the neck of the retort where it enters the tube of the condenser.

(7.) *Lamp and Retort-Holder.*—A large Bunsen burner affords a convenient source of heat during the distillation. As will be explained, we apply the naked flame to the retort. The retort-holder should be very steady and massive. We are in the habit of using a very well-known description of clamp made of metal, and lined with cork where it clips the neck of the retort. The incline of the retort-holder must be carefully adjusted to the incline of the condenser, so that the retort may be retained in position without any unnecessary pressure. The employment of a ring to support the retort from below is not to be recommended. Much of the ease of the working of the process depends upon the proper mounting of the retort, which ought to admit of the easy removal of the retort, and easy remounting.

(8.) *Glass Cylinders for Nessler Test, or Nessler Glasses.*—These should be of perfectly white glass. In my own laboratory the Nessler glasses are cylinders, 17 centimetres in height and 4 centimetres in diameter. They are marked with a file-mark at 50 c. c. capacity. From half-a-dozen to a dozen are necessary. We use also a white porcelain tile for them to stand upon when they are used.

(9.) 100 *c. c. Flask and a* 250 *c. c. Flask.*—These flasks are used for measuring out the quantity of sewage taken for analysis. They have only one file-mark at the 100 c. c. or 250 c. c. capacity.

(10.) *The Measure for Solution of Potash and Permanganate of Potash* is a convenient glass with a simple mark at 50 c. c.

capacity. To pour well is an essential qualification that such a glass should possess. We are in the habit of using a thick glass vessel which is an apothecary's dispensing four-ounce measure, and which was bought in an ungraduated state.

(11.) *A Graduated Burette*, divided accurately into cubic centimetres, and provided with a glass stopcock, is used for measuring out the dilute standard ammonia. It is held by any convenient holder.

(12.) *The Pipette for Nessler Reagent* is made of a piece of glass tube, and requires just one file-mark at the 2 c. c. capacity.

Bottles are required to hold the different solutions. It is of importance that the bottle holding the solution of potash and permanganate of potash should pour well. A glass funnel is also required.

The convenience of having a water-supply and sink close at hand will be readily appreciated. It will also be found to be advantageous to keep a table, or part of a table, appropriated exclusively to these analyses, and to appropriate a set apparatus to them. Thus the funnel, the 100 c. c. flask, the retort, the condenser, burette, pipette, and Nessler glasses, should not be used for anything else.

One very important matter in testing of this order of delicacy is the cleaning and washing out of the apparatus, and it should be borne in mind that all glass surfaces which have been exposed to the air for any length of time are liable to contract traces of ammonia from the air; and the rule is to wash out with clean tap-water immediately before use. Distilled water need not be used for these washings—an ordinary town-water will do—but there should be no

stint of the quantity of water. The analysis is performed in the following manner:—

The retort having been washed out with a little strong acid (either hydrochloric or sulphuric acid), is then washed out with good tap-water, until the few drops which drain out do not taste acid. It is then mounted in its holder and properly connected with the Liebig's condenser, either by means of a wide india-rubber tube, or by means of a little writing-paper.

The quantity of sewage or sewage-effluent which is generally most convenient is 100 c. c., and it will be found advisable to mix it either with 200 c. c. of good distilled water, or of good town-water of known quality.

First 200 c. c. of distilled water, or of tap-water of known quality, are poured into the retort before putting in the sewage, and boiled before the sewage is poured in. The 100 c. c. of sewage is measured in the 100 c. c. flask and poured through the funnel into the retort. The stopper or cork, which must be kept scrupulously clean, is put into its place in the retort, and the Bunsen lamp is lighted, and the flame applied externally to the naked retort. The retort must be thrust right down into the flame, which, however, must not play upon the surface of the retort higher than the level of the liquid within the retort. In a few minutes the contents of the retort will begin to boil, and the water will begin to distil over. The distillate is to be collected in the glass cylinders for the Nessler test.

All sewages and most sewage-effluents contain much ready-formed ammonia, and that has to be provided for. And it is advisable to distil off 150 c. c., and put that aside in a flask or clean-stoppered bottle for *future Nessler-*

ising. After the 150 c. c. have come over, the receiver is to be changed, and about 20 c. c. is to be distilled into a Nessler glass and *Nesslerised,* which will be explained farther on.

If the result of the Nesslerising be satisfactory (which will be explained farther on), the distillation is stopped for a moment; and fifty cubic centimetres of the "solution of potash and permanganate of potash," which has been described, is then to be poured into the retort through a wide funnel, and the distillation proceeded with.

At this stage of the operation it is often necessary to shake the retort gently to avoid bumping, and the lamp requires management. The distillation must be slowly continued until 50 c. c. have distilled over into a Nessler glass. Finally, at least 25 c. c. is further distilled, and the distillation may then be stopped, and the apparatus left standing until it is required for another analysis.

Nesslerising is the operation of finding the strength of dilute solutions of ammonia by help of the Nessler test—a test discovered by a chemist named Nessler. The preparation of the Nessler reagent has already been described in detail. Let it be required to tell how much ammonia is contained in 50 c. c. of distillate contained in one of the cylinders above mentioned.

For this purpose 2 c. c. of Nessler reagent are dropped into the 50 c. c. of distillate. This is best done by aid of the appropriate 2 c. c. pipette above mentioned. The pipette also serves as a convenient stirrer, to stir up the liquid after the addition of the Nessler reagent to it. If the 50 c. c. of distillate contain any ammonia, it will soon after the addition of the Nessler reagent, as just described, assume a

rich brown colour; and the more the ammonia, the deeper the colour.

The next step is to imitate the depth of colour given by the distillate. In order to do so, a clean cylinder is taken, and into it is dropped a certain measured volume of the standard solution of weak ammonia, which is filled up with distilled water to the 50 c. c. mark on the cylinder. Two c. c. of Nessler reagent is then dropped into it by means of the pipette, and the whole is very thoroughly stirred up. The 50 c. c. of distillate in its appropriate cylinder, and the 50 c. c. of water containing the standard ammonia, are then placed side by side on a white surface (a white porcelain tile answers very well), and carefully looked through, and a judgment is arrived at as to which is of the deeper colour. If they be of equal depth, the Nesslerising is accomplished, inasmuch as the quantity of ammonia required to imitate the colour, which the Nessler reagent imparts to the distillate, is the quantity of ammonia in the distillate. If the two solutions be not of equal depth, another standard must be made up with water, dilute standard ammonia, and Nessler reagent, and another comparison must be made.

With a little practice Nesslerising becomes very easy.

In the course of the analysis it will be perceived that ammonia is to be looked for at two stages: firstly, before the addition of the potash and permanganate; and secondly, after the addition of the potash and permanganate. The ammonia which comes over in the first stage is the "free ammonia," and that which comes over in the second stage is the "albuminoid ammonia."

The advice has been given to put aside the first 150 c. c. of distillate for future Nesslerising. Owing to the large

proportion of free ammonia in sewages, it frequently happens that when one-third of this first distillate—*i.e.* 50 c. c.—is mixed with the 2 c. c. of Nessler test, there is *precipitation.* If there were *three milligrammes* in the 150 c. c. of distillate which had been set aside, there would most likely be precipitation on adding the Nessler reagent to 50 c. c. of the distillate. The experiment might be tried, and if precipitation took place, then another experiment would have to be made as follows :—

A small portion of the 150 c. c. is measured out and placed in a Nessler glass, and diluted with pure distilled water. Conveniently the small portion might be 15 c. c. (which is one-tenth of the 150 distillate). The 15 c. c. is put into a Nessler glass, filled up to the 50 c. c. mark with distilled water, and then the 50 c. c. of diluted distillate may be Nesslerised.

Let us suppose that the result of this Nesslerising was .45 milligrammes of ammonia. Then the yield of free ammonia in the experiment would be 4.50 milligrammes per 100 c. c. of the sewage.

And in terms of milligrammes per litre of sewage (parts per million), the result would be 45.00 milligrammes of free ammonia.

The object of collecting separately 20 c. c. of distillate after distilling the half of the liquid is to make sure that all the free ammonia has come over. If on Nesslerising the amount of ammonia does not exceed .05 milligramme, the result is satisfactory, and the operator may proceed to add the alkaline permanganate.

In this place we consider ourselves bound to state in the most explicit manner, that the application of the

ammonia method to sewage and strong sewage-effluents is by no means an easy experimental task; and we would advise no one who has not had some experience in water-analysis to undertake the performance of the task.

The composition of raw sewages, as indicated by the ammonia method when correctly carried out, appears to average: free ammonia 50.00 to 60.00 milligrammes per litre of sewage.

Albuminoid ammonia 3.00 to 4.00 milligrammes per litre of sewage.

In some extraordinary cases, as, for instance, where manufacturing operations come into play, the free ammonia appears to have fallen as low as 24 milligrammes per litre, and the albuminoid ammonia has risen to 8.00 milligrammes per litre.

Typical sewages, as may be seen on making the calculation from the data provided in our Introduction chapter, should contain 61.2 milligrammes of free ammonia per litre.

It is very difficult to calculate *synthetically* the albuminoid ammonia in typical sewage. If we restrict our view to that portion of the excreta which is soluble in water when it leaves the human body, the figure for the albuminoid ammonia in typical sewage would come out very small; but if we enlarge our view and take in the insoluble substances present in the fæces, then the figure might rise even to 15 milligrammes per litre of typical sewage; but that could only happen if there were no destruction of the organic matter by fermentative change and by oxidation.

As we have already remarked, the ascertainment of the

true figure for the albuminoid ammonia in sewages and sewage-effluents involves some practical difficulties, and we fear that much of the work put forward by our chemical brethren is invalid. We suspect that serious errors, both in the direction of an over-estimate and an under-estimate have been made on many occasions when sanitary officials have employed the ammonia method in the examination of sewages and sewage-effluents.

It will be at once understood that an over-estimate of the albuminoid ammonia is inevitable when free ammonia is mistaken for it; and it must be intelligible to every one that inasmuch as there is fifteen to twenty times as much free ammonia as albuminoid ammonia in sewages, great care is demanded in order that none of the "free" is mistaken for the "albuminoid."

We strongly suspect, also, that the sanitary official is very much in the habit of risking destruction of the albuminoid substance by an injudicious manner of performing the operation, and we very much doubt whether sufficient care is usually taken to ensure the completeness of the oxidation of the albuminous substances.

In the year 1874, in the third edition of the "Water-Analysis," in which for the first time there appeared a special chapter on Urine and Sewage, one of us has described a modification of the ammonia method which is specially adapted to deal with some of the experimental difficulties which beset the chemical examination of sewages.

Slightly modified to meet the special difficulties of the case, the method will now be described.

A solution of caustic potash in good distilled water is made, the proportion being 0.5 gramme of potash to 100 c. c.

of water. Of course the solution requires to be tested, so as to make sure that it contains no albuminoid matter.

Into a clean flask-retort, capable of holding 250 c. c., we place 100 c. c. of this potash solution, and heat till the liquid begins to boil, then the lamp is removed and 100 c. c. of the sewage is poured into the hot flask.

The flask-retort is now to be heated in an oil-bath, and is neatly connected with a small Liebig's condenser, as

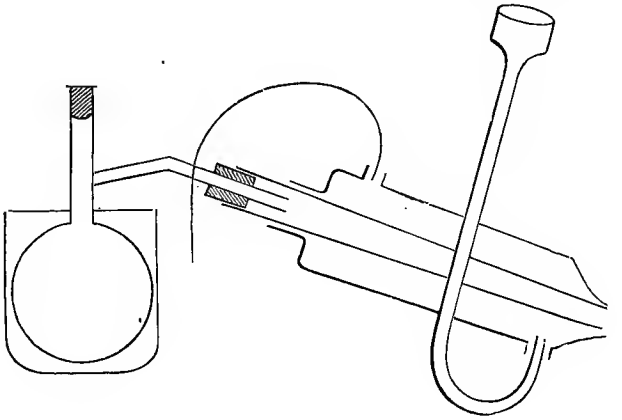

FIG. 4.

shown in the accompanying rough sketch. The temperature of the oil-bath is raised to 150° C., and the distillation is commenced and continued until nearly all the liquid has distilled.

When the contents of the flask-retort appear nearly dry, *i.e.* when a temperature of 150° C. has been maintained for a short period in the interior of the flask, the temperature should be lowered. This is done by getting the flask out of the hot oil or spermaceti, and either the oil-bath

may be lowered down away from the flask, or else the flask, which is to be maintained in firm connection with the Liebig's condenser, may be raised out of the oil.

If the Liebig's condenser be held by a proper kind of clamp, made of metal lined with cork, and very firm and convenient, this raising up of the apparatus will be found to be quite easy.

In a minute or two the flask-retort will have become cool enough to admit of the introduction of 20 c. c. of distilled water free from ammonia; and that having been done, the oil-bath is again applied to the retort, and the distillation proceeded with. This is continued almost to dryness, and the distillate is mixed with the first distillate, which on proper Nesslerisation furnishes the free and *ureal* ammonia yielded by the 100 c. c. of sewage.

The flask-retort is again taken out of the oil-bath, allowed to become somewhat cool, and then 50 c. c. of the solution of potash and permanganate is poured into it.

Finally, it is again placed in the oil-bath, which is maintained at 150° C., and the distillation is continued to dryness in the oil-bath. The distillate contains all the albuminoid ammonia, and should be Nesslerised, as has been explained.

The test of good working is that practically the same figure should be given for albuminoid ammonia by the two modifications which we have described.

In conclusion, we should most strongly advise that whenever a sewage-effluent shows very little albuminoid ammonia, the analysis should be repeated on a larger scale; and that a half-litre should be operated upon, just as if it were a drinking water.

CHAPTER VI.

THE MOIST COMBUSTION PROCESS APPLIED TO SEWAGE AND SEWAGE-EFFLUENTS.

THIRTY years ago, Frankland made an attempt to measure the total organic matters in drinking-water by resorting to an elementary organic analysis of the residue left on evaporating down a known volume of the water. The attempt was not attended with success, inasmuch as the extreme minuteness of the quantity of organic matter in a litre of drinking-water rendered the determinations impracticable and illusory.

In the case of sewage and many sewage-effluents, the proportion of organic matter is very much larger than in drinking-water.

In typical sewage there would be about 300 milligrammes of organic matter per litre, if the fermentation were restricted to the ureal fermentation, and if there were no oxidation of the sewage. As a matter of fact, the investigation of sewage taken at the outfall of the sewer discloses less than that quantity of organic matter. Such a quantity of organic matter as 100 milligrammes in a litre—and more especially since there are no nitrates in sewage—would come well within the scope of elementary organic analysis; and we see no *insuperable objections* to the application of the method of elementary organic analysis to sewage and many sewage-effluents.

To investigate sewage in that manner would, however, call for a high degree of manipulative skill, and would be very troublesome. We are of opinion that substantially the same results may be obtained much more easily by another method which we shall presently describe. Our method consists in converting into carbonic acid all the carbon, or nearly all the carbon, existing in organic combinations in the sewage, and all the hydrogen into water (except that which escapes with the nitrogen in the form of ammonia); and the measurement which we perform is a measurement of the total oxygen consumed in effecting these transformations. The agent which we employ in order to bring about these transformations is permanganate of potash: the manner in which we use the permanganate is totally different from that in common use.

Before describing our method, to which we gave the name of "The Moist Combustion Process" in the year 1878, we will discuss the common permanganate process, which—very much as it was described by the late W. A. Miller in the year 1865 and by Frankland in the year 1866—continues in use at the present time.

The characteristic details of the common permanganate process are that the permanganate solution is applied *to the water or sewage in the presence of a comparatively large proportion of acid;* that the action is carried on at *ordinary atmospheric* temperatures, or at temperatures *not so high as blood heat;* and that the action is *prolonged for several hours.*

The datum to be observed and recorded is how much permanganate is destroyed by a given volume of sewage. Four parts of the permanganate of potash contain one part of active oxygen. If, then, the weight of the permanganate be

ascertained, the actual quantity of oxygen which has been consumed admits of ready calculation by the simple arithmetical operation of dividing by 4.

In making observations of the quantity of permanganate used up, there are two varieties of procedure. One is the simple plan of adding the solution of permanganate little by little, as long as the red-purple colour seems to fade, and making a record of the quantity of the solution which has been added.

The other procedure is by first adding an excess of the permanganate, and afterwards ascertaining how much excess has been added by employing a standard solution of hyposulphite of soda in presence of iodide of potassium and starch paste, as was described by Miller in 1865 and attributed by him to Vernon Harcourt.[1]

This common permanganate process of the years 1865 and 1866, as we have already remarked, is widely used in this country even at the present time. Slight and trivial variations, which do not touch its essential defects, have, it is true, been introduced and paraded before chemists, but substantially, and for all practical purposes, it remains the same. We are not writing at all too strongly when we assert that the records of chemical analysis disclose no worse method than this common permanganate process as applied to sewage and sewage-effluents. It fails in almost every imaginable way. The weak solution of permanganate which is employed, as we have said, in acid solution is almost devoid of action upon many of the commonest and most abundant organic compounds. Upon cellulose, for instance,

[1] *Vide* W. A. Miller's paper in the *Journal of the Chemical Society* for the year 1865, pages from 120 to 123.

it exerts so little action, that the standard permanganate solution (strength one milligramme of active oxygen in one cubic centimetre) may be filtered through clean white filter-paper without suffering any appreciable change in strength.

We have just verified this fact in our laboratory. Our standard solution, prepared by dissolving four grammes of crystals of permanganate of potash in one litre of good freshly distilled water, contains one milligramme of active oxygen in one cubic centimetre. We have filtered 50 c. c. of this solution through a common white filter-paper weighing about 650 milligrammes. We have also passed the liquid a second time through this same filter-paper, and we have tested the strength of the twice-filtered filtrate.

There is no sensible alteration in strength: both the filtered and unfiltered liquids require the same volume of the same tin-solution in order that the red-purple colour may be caused to vanish.

The inactivity of permanganate in presence of a relatively large excess of free acid was published thirty years ago. In 1868, Frankland—after having used the common permanganate process in his capacity of official analyst of the London water-supply—abandoned the common permanganate process, and, in doing so, placed on record the most striking illustrations of the utter futility of that process.

Frankland prepared solutions of several organic substances, making the strength of the solutions to be 30 milligrammes of organic matter in one litre of the solution. These solutions were then submitted to the action of the permanganate in acid solution in the usual manner. The experiments were published in the *Journal of the Chemical Society* for the year 1868, on page 83. Gum-arabic be-

haved in this wise :—In ten minutes the amount of oxygen consumed was registered as 0.102 milligramme, instead of 35.500 milligrammes. In six hours the registered consumption of oxygen was only 0.350 milligramme.

Cane-sugar exhibited this inactivity of the permanganate even more strikingly, if that be possible. In ten minutes the consumption of oxygen was found to be 0.064 milligramme instead of 33.700 milligrammes ; and in six hours 0.152 instead of 33.700.

According to Frankland, therefore, a six-hours' contact of the weak sugar-solution with acid permanganate solution, at the ordinary temperature of the air, does not bring about so much as the one two-hundredth ($\frac{1}{200}$) of the theoretical oxidation.

Frankland published also an experiment on the weak solution of alcohol, in which experiment the consumption of oxygen in ten minutes was set down as 0.093, and in six hours as 0.164 instead of 62.600 milligrammes. No one has ever ventured to call these results in question—not even Sir Henry Roscoe has called them in question, and at the present time Sir Henry Roscoe employs the common permanganate process in order to ascertain the amount of organic matter in sewage and sewage-effluents.

The demonstrated inactivity of the permanganate in acid solution would doubtless have been followed by the abandonment of the common process, if it had not been for the circumstance that the chemistry of manganese is highly complex, and that permanganate solution is sometimes singularly active and seemingly capricious. Although pure sugar solution is almost absolutely stable in presence of permanganate in acid solution in the cold, yet there are

many organic substances which are rapidly attacked under such conditions. Oxalic acid is rapidly, and indeed sometimes instantaneously, attacked and oxidised down to carbonic acid. Fresh urine, even that which is perfectly fresh and acid to test-paper, decolourises acid permanganate freely and instantaneously. Many inorganic substances are also rapidly attacked by permanganate in acid solution. Peroxide of hydrogen, curiously enough, is rapidly and indeed violently attacked. Sulphites, hypo-sulphites, sulphuretted hydrogen, nitrites, ferrous salts and stannous salts instantly decolourise acid permanganate solutions.

The behaviour of manganous salts towards acid solutions of permanganate is very remarkable, and assumes importance from the circumstance that manganous salts necessarily result from the exertion of the oxidising power of the acid permanganate; and indeed ignorance of the peculiarities in the behaviour of manganous salts lies at the root of the prevalent misuse of the acid permanganate solution.

It is many years since a chemist—we believe that the chemist was Vernon Harcourt—first called attention to a curious fact in connection with the titration of a solution of oxalic acid by means of acid permanganate.[1]

If a pure solution of oxalic acid be taken and mixed with a little pure dilute sulphuric acid, the addition of a pure solution of the permanganate in quantity sufficient to destroy one-quarter of the oxalic acid will not occasion any immediate chemical action, and the deep red-purple colour may remain for a long time, certainly for a quarter of an hour. But if a little of a solution of manganous chloride be added, then there is an immediate change, and the

[1] Vide *Journal of Chemical Society*, 1867, page 465.

liquid becomes deep brown, light brown, and after the lapse of a few minutes the colour vanishes altogether. On continuing the addition of the permanganate, there is disappearance of the red-purple, and then the stages of deep brown, light brown, and ultimately complete bleaching, until the point is reached at which the oxalic acid has been consumed; and when that point has been reached the bleaching ceases, and if the additions of permanganate go on, there is an abundant deposit of the brown hydrated binoxide of manganese.

The following very instructive experiment, recently carried out in our laboratory, exhibits in a very striking manner some of the peculiarities of the action of manganous salts, and appears to us to illustrate the absolute futility of the common permanganate process.

A solution of pure crystals of manganous chloride, $MnCl_2 2H_2O$, was prepared containing one gramme of the crystals in one litre of water.

50 c. c. of good distilled water was placed in a clean glass beaker. To this was added 1 c. c. of diluted sulphuric acid containing about 200 milligrammes of real sulphuric acid, H_2OSO_3. Then we added 5 c. c. of the standard permanganate solution containing in each cubic centimetre 1 milligramme of active oxygen; and lastly, we dropped into the liquid 5 c. c. of the solution of manganous chloride.

There was no immediate change in the appearance of the contents of the beaker; but after the lapse of a few minutes the brightness of the permanganate was impaired. Gradually turbidity set in, and in the course of twenty minutes colour had left the liquid, and the contents of the

beaker became an almost absolutely colourless liquid with brown powder floating in it. In the course of four or five hours the brown powder settled down at the bottom of the beaker.

The point in this experiment is that one atom of metallic manganese in the shape of the chloride has decolourised nearly four atoms of metallic manganese in the condition of permanganate of potash, and the brown precipitate which settled down consisted, in all probability, of hydrated binoxide united with permanganate.

In the course of other experiments of a similar character, we have observed that the proportion of permanganate carried down by the binoxide is subject to great irregularity.

The practical bearing of these facts must be obvious. If, as we have proved, the presence of the manganous salt in an acid solution of the permanganate occasions the slow precipitation of much more than its equivalent of the permanganate, and the consequent loss of colour from the solution, the attempts to arrive at the amount of organic matter by taking note of the slow consumption of the permanganate must be utterly futile.

We are quite aware that a desperate attempt will be made to parry this criticism by maintaining that, although colour may be gone, the unused active oxygen is preserved intact in the precipitate, and is to be arrived at by resorting to Harcourt's modification and employing hyposulphite and starch paste and iodide of potassium.

To any one who should seriously contemplate such a defence of the process, I would quote from Miller's paper of 1865, wherein, at the end of the description of the

Harcourt modification, there are the ominous words, "The burette must be read off the instant the colour disappears, as on standing the blue tint returns."

We have experimented upon these brown precipitates, and have resorted to the use first of iodide of potassium and then of the hyposulphite and the starch paste indicator. We find that though the brown powder may possibly contain most of the unconsumed active oxygen, its physical condition places difficulties in the way of extracting all the active oxygen. *The blue tint does indeed return on standing.*

In fine, what we mean to make manifest is, that the striking inertness of the acid permanganate in presence of weak solutions of many commonest organic substances—which has been an *acknowledged* scientific fact for thirty years—is ignored in England at the present time; and that the ignoring of this inertness of this acid permanganate is maintained by faulty experimental workmanship.

Chemists are indebted to Mr. Carter Bell for bringing prominently forward how urgent is the need for a reform in the official employment of Forchhammer's reagent for sanitary purposes. In a paper of his, published about a year ago, entitled "On the Oxygen Test for Sewage and Sewage-effluents as carried out in the Laboratory of the Mersey and Irwell Joint Committee," we read as follows:—

"During the last few months many samples of effluents have been taken by the Joint Committee from the Salford Corporation Sewage Works, and have been examined by the permanganate test. When the results were reported to the Corporation, they were almost invariably higher than those I reported, sometimes as much as 40 per cent."

And the following examples are given :—

Milligrammes of Oxygen required to Oxidise the Organic Matter in One Litre of Sewage-effluent.

	I.	II.	III.	IV.
Sample 1 . . .	55.7	42.8	32.8	34.3
„ 2 . . .	32.8	27.1	25.7	20.0
„ 3 . . .	62.8	40.0	48.6	25.7
„ 4 . . .	44.3	...	32.9	...

Our readers will doubtless sympathise with Mr. Carter Bell when he remarks that "it is not pleasant to have one's analyses constantly in dispute," and will appreciate how disastrously the official misuse of the permanganate might mislead our public authorities when they are called upon to deal with sanitary questions.

Columns I. and II. express the results of the examinations by the Joint Committee, and columns III. and IV. are the figures given by Mr. Carter Bell. (We have translated the results, and present them in terms of milligrammes per litre.)

The Mersey and Irwell Joint Committee are responsible for their own analyses, and the details of the permanganate test, as worked in their laboratory, have been published officially.

These details are now set forth as follows :—

Permanganate Test.

"Process for the estimation of oxidisable organic matter as measured by the action of an acid solution of permanganate of potash on the sewage-effluent.

"Two determinations are made, viz., the amount of oxygen absorbed during three minutes, and that absorbed

during four hours, both determinations being made at a temperature of about 60° F.

"Standard solutions required :—

"1. H_2SO_4 solution.—1 part by volume of pure H_2SO_4 + 3 parts pure distilled water. Permanganate solution is added until a faint red tinge remains for some hours.

"2. $KMnO_4$ solution.—0.395 gramme per litre of pure crystallised $KMnO_4$.

"3. KI solution.—1 part KI to 10 parts of distilled water.

"4. $Na_2S_2O_3$ solution.—4 parts $Na_2S_2O_3$ by weight dissolved in a litre of water distilled.

"5. Starch-water.

"Process.—Take 70 c. c. of the sewage-effluent in a 5 to 8 ounce stoppered bottle, add 10 c. c. H_2SO_4 solution + 50 c. c. $KMnO_4$ solution. Allow to stand four hours. If during this period the permanganate colour is much faded, another 50 c. c $KMnO_4$ solution is added, so as to always have an excess of permanganate present At the end of four hours a few cubic centimetres of potassium iodide solution are added, and the iodine liberated titrated with the $Na_2S_2O_3$ solution, using starch for the end reaction.

"Each day a blank experiment is made with 70 c. c. distilled water + 10 c. c. H_2SO_4 + 50 c. c. $KMnO_4$ so as to standardise the hyposulphite.

"The three minutes' test is determined by directly adding $KMnO_4$ solution from a burette to 70 c. c. sewage-effluent + 10 c. c. H_2SO_4, the colour of the permanganate forming a sufficiently delicate indicator."

Mr. Carter Bell has also published the details of his work,

His solution of hyposulphite of soda is not so strong as that used by the Joint Committee, and his starch-water is specially prepared: otherwise the solutions are the same as those of the Joint Committee. There is very little difference in the working. Mr. Carter Bell operates upon 20 c. c. of sewage-effluents (instead of upon 70 c. c.), and he dilutes with 50 c. c. of distilled water, and he takes a diminished volume of the permanganate solution. Like the Joint Committee, he operates at ordinary temperatures, and the period of contact is four hours.

That one and the same effluent should consume 62.8 milligrammes of oxygen per litre in the laboratory of the Joint Committee, and only 25.7 in the laboratory of Mr. Carter Bell, illustrates the utter worthlessness of the common permanganate process as it is worked under the most favourable conditions at the present time.

Twenty years ago, in the year 1878, as we have already mentioned, we endeavoured to provide sanitarians, and chemists in general, with a method which should not be open to the objections and difficulties besetting the common permanganate process. We will now describe that method.

Its distinguishing characteristics are:—

(1) That the permanganate is made to act upon the organic substance in a strongly alkaline solution.

(2) That the oxidation takes place at the boiling-point of water, or indeed sometimes at a few degrees above the ordinary boiling-point of water.

(3) That, comparatively speaking, it is a quick process, the actual oxidation of the organic substance taking place in from *a quarter* to *half an hour*.

(4) That although the actual work of destruction by

oxidation of the organic substance is carried on in the alkaline solution, the record of the strength of the permanganate, both before and after the oxidation, is kept in the acid solution.

The name which we gave to our method, the *Moist Combustion Process*, is justified by the circumstance that by employment of it we achieve the burning down of most organic substances into the final products of combustion, *i.e.* into carbonic acid and water.

In the moist combustion process, instead of cane-sugar absorbing less than $\frac{1}{100}$ of its own weight of oxygen, an absorption of fully its own weight of oxygen is brought about.

The practical details of the moist combustion process are as follows:—

Four solutions are required.

(1) Solution of Permanganate: strength, one cubic centimetre containing one milligramme of active oxygen: 4.00 grammes of crystals of permanganate of potash are dissolved in one litre of distilled water.

(2) Solution of Protosulphate of Iron: strength, one cubic centimetre absorbing one milligramme of active oxygen: 35 grammes of crystals of ferrous sulphate are dissolved in water, 50 c. c. of strong sulphuric acid (oil of vitriol) are added, the solution is cooled and diluted to one litre.

(3) Solution of Caustic Potash: 100 grammes of potash are dissolved in a litre of water.

(4) Solution containing Sulphuric Acid: 100 c. c. of oil of vitriol are mixed with one litre of water.

The apparatus requisite is a flask or retort, and an arrangement for boiling, a 250 c. c. measure, a 5 c. c.

pipette to discharge 5 c. c., a 25 c. c. burette graduated to 0.2 c. c., and a 50 c. c. measure.

The operation is performed thus :—

The retort employed for the ammonia process may be used, and having been cleaned and mounted as if for the ammonia process, is charged with 250 c. c. of the sewage or sewage-effluent to be examined. Before beginning to distil, 50 c. c. of the solution of caustic potash is dropped into the sewage contained by the retort, and then 50 c. c. of the solution of permanganate are very carefully measured, and likewise dropped into the retort, which is then heated and its contents rapidly distilled until about 100 c. c. have distilled over. That having been done, the heating is stopped, and the observation is made that the liquid remaining in the retort retains a pink colour. Then 50 c. c. of the solution of sulphuric acid are dropped into the retort and shaken up with the contents of the retort. Then 50 c. c. of the iron solution are to be dropped into the retort, and in a few minutes the liquid will become quite colourless. That having been attained, the solution of permanganate of potash contained in the graduated burette is carefully dropped into the liquid, and the point is accurately noted at which the red colour just begins to be permanent.

The following data will thereby be obtained :—

(*a*) Total number of c. c. of permanganate used up.

(*b*) Total number of c. c. of permanganate used up by the iron solution.

The difference between these figures is the number of c. c. of permanganate consumed by the organic matter in one quarter of a litre of sewage, or the number of milligrammes of active oxygen consumed by the organic matter in a

quarter of a litre of the sewage. An example will render this description intelligible.

A sewage-effluent was operated upon as follows :—

Volume of effluent taken . . .	250 c. c.
„ „ solution of potash . . .	50 c. c.
„ „ permanganate solution . .	50 c. c.

which were poured into the retort, and the mixture was distilled until 80 c. c. had distilled over. Then the lamp was removed, and the retort allowed to cool down a little. Next the observation was made that the contents of the retort were deep-coloured, indicating a considerable excess of the permanganate; and 50 c. c. of the solution containing sulphuric acid was added, also an accurately measured 50 c. c. of the iron solution was added, and the contents of the retort were shaken up to cause thorough mixture. By that treatment the liquid contents of the retort became clear and almost colourless, the slight tinge of colour being the colour of ferric salts. Lastly, permanganate solution was dropped into the retort until a red tinge was obtained. The quantity of permanganate required to occasion this colouration was 4.0 c. c. A testing of the strength of the iron solution was made, and 10 c. c. of iron solution was found to require exactly 9.1 c. c. of permanganate.

From these observations the following record was drawn up :—

Volume of sewage-effluent taken . . .	25.0 c. c.
Total permanganate used	54.0 c. c.
Permanganate used by the 50 c. c. of iron solution	45.5 c. c.
Therefore permanganate consumed by the organic matter in 250 c. c. of sewage-effluent	8.5 c. c.

One litre of this sewage-effluent consumes 34 c. c. of permanganate or 34 milligrammes of oxygen.

Here the remark may be made, that in using the permanganate for the final measurement (that is to say, when the 4.0 c. c. was read off), the reading must be immediate, and not after the lapse of time.

The moist combustion process, as just described, will be found to involve no practical difficulties. It may be carried out either on a larger or a smaller scale; but we prefer the quarter-litre in the case of sewages or sewage-effluents, and we think that there would be an undoubted advantage in avoiding any departure from that scale of operation. The final result should invariably be given in milligrammes per litre or parts per million.

We do not consider that any good purpose can be served by distinguishing between the quick and slow oxidation by permanganate. Such a distinction is delusive.

The oxygen consumed in moist combustion may be taken as being an approximation to the actual weight of the organic matter in the sewage or sewage-effluent, and is a very important datum.

In raw sewage we have found as much as 154 milligrammes of oxygen required by the litre, and in an extreme case, when the sewage was very weak, we once found as little as 48.8 milligrammes.

Obviously, whether the sewage has been allowed to settle and deposit a precipitate, or whether it has been shaken up so as to diffuse the precipitate, must make a considerable difference in the figure given by moist combustion.

In a sample of sewage recently examined, the settled

sewage furnished the result 80.0, and the shaken-up sewage 107.

In closing this chapter we may remark, that instead of a ferrous solution we have sometimes used a solution of tin—an acid solution of stannous chloride. Inasmuch as these solutions are very liable to atmospheric oxidation, they should be frequently tested, and due allowance made for the altered strength. Further explanations and illustrations are given in the appendix under the heading of Chemistry of Manganese.

CHAPTER VII.

THE TOTAL SOLID RESIDUE, ITS AMOUNT AND EXAMINATION —GENERAL STATEMENT OF ANALYTICAL RESULTS.

When sewage or sewage-effluent is evaporated, it loses water, ammonia, carbonic acid, and sulphuretted hydrogen, if any be present, and small traces of volatile organic matters, and there remains behind a residue consisting of the mineral matter existing in the sewage, together with such organic matter as escapes decomposition, and any water of hydration or crystallisation that may be capable of withstanding the heat to which the residue is subjected.

The general practice is to evaporate in the water-bath or steam-bath at the boiling-point of water, and to maintain the apparently dry residue at that temperature for a short time, then to cool and weigh.

In the case of sewage or sewage-effluent, the volume most generally convenient is 250 c. c., which is measured in a suitable graduated flask or cylinder. A vessel with one solitary marking has an obvious advantage. A platinum dish or else a nickel dish holding about 120 c. c. will be found to be a suitable vessel as a receptacle for the sewage during the evaporation. Before being used, this dish must be cleaned and made bright, wiped and carefully weighed, and its weight noted down.

Then it must be placed in the water-bath, which may be either a glass beaker of the proper size, or a copper

vessel with a hole or holes in its cover to admit of the reception of the dish. (Such a bath may be procured from most of the dealers in chemical apparatus.)

The bath may be heated by means of gas, and a Bunsen-burner will answer very well. Having heated the water in the bath to boiling, the operator may then pour a portion of the measured 250 c. c. into the dish, care being taken not to pour too much, so as to over-fill the dish. After the evaporation of the greater part of the contents of the dish, more liquid may be poured in, and so on, till the liquid has all evaporated away. The residue having become apparently dry, a short time must be allowed to elapse in order to ensure complete drying before removing the dish from the bath. The outside of the dish is to be wiped dry with a cloth, and then is to be rapidly cooled and weighed.

The difference between the two weighings is the weight of the total solid residue left by the evaporation of 250 c. c. of the sewage. The following is an example in point:—

250 c. c. of sewage-effluent taken.

Dish + residue (dry at 100° C.) .	= 65.284 grammes.
Dish	= 65.089 „
	= .195
195 multiplied by 4 . .	= 780

∴ 780 milligrammes is the residue left by one litre of the sewage-effluent.

In carrying out these operations, the operator will experience difficulty in arriving at a satisfactory weighing of the dish with its adherent residue, because even whilst the dish is on the pan of the balance it will alter in weight: it will attract moisture. In order to obviate this difficulty, it is necessary to protect the residue by means of a cover. We

find that the best cover is an upper dish fitting almost air-tight into the lower dish, and leaving a meniscus-shaped air-space between the two dishes. Pairs of dishes, which should be weighed together, are to be bought of Messrs. Baird & Tatlock of Hatton Garden, E.C.

The manner of using the pair of dishes will be obvious, but perhaps a caution will be useful. The upper dish should not be cold when it is inserted into the lower dish containing the dry residue. It should be hot and dry when inserted, and not cold, and presumably moist.

We have recommended that 250 c. c. of the sewage should be operated upon, and in general such a quantity is the safest. An unusually expert and skilful operator may possibly prefer to take 100 c. c.

Having obtained the total solid residue dry at 100° C., the question arises as to further investigation of the nature and composition of that residue.

One point crops up at once. What is the possibility of measuring the amount of organic matter by the well-known and time-honoured method of igniting and noting the loss on ignition?

The reply to that question is, that such a measurement is quite practicable, and that when certain precautions are taken the measurement is a good one.

The case of sewage and sewage-effluents differs somewhat from that of drinking-water by reason of the larger proportion of organic matter, and more especially of the larger proportion relatively to the mineral matter.

The excreta which, on mixture with water in the sewer, constitute the sewage, would, if they suffered no change, produce a liquid emulsion containing as much, or even

sometimes more, organic than inorganic matter. Even after the ureal fermentation has run its course in the sewer, there remains sufficient organic matter in the sewage to admit of the application of the method of ignition.

In resorting to this measurement of the organic matter in sewages or sewage-effluents, some precautions are necessary. These liquids being of a very alterable nature, must not be subjected to a slowly rising temperature without being first treated with some reagent, with the power of stopping fermentative change. The 250 c. c. of sewage should be shaken up with 5 c. c. of benzene or toluene, for instance, and in contact therewith it may be afterwards set to evaporate in the water-bath. The drying, cooling, and weighing of the residue having been accomplished, the ignition may be carried out by the aid of the flame from the Bunsen-burner. The ignition should be very gentle: the lid should then be put on, the cooling quickly accomplished, and the final weighing made.

The difference between the weight before and after ignition—the "*loss on ignition*"—affords a guide to the real amount of *organic* matter in these sewage-residues, and, when used with judgment and discrimination, provides either a confirmation or a reason for distrust, as the case may be.

As to the further investigation of the solid residue, an instructive determination is that of the soluble and insoluble portions of the residue. A small quantity of distilled water, about 40 c. c., is added to the residue and kept in contact with it for two or three hours, then the solution is filtered through a very small filter, which is washed.

The solution is evaporated to dryness, and the residue

weighed, and so the soluble residue is found. The insoluble residue may likewise be determined by drying up the residue left in the dish and on the filter-paper, which should be burnt, and the ash added to the residue in the dish.

In the instance of the total solid residue of 780 milligrammes per litre of sewage-effluent, the insoluble residue weighed 250, and the soluble 465 milligrammes.

We have therefore:—

	Milligrammes.
Soluble residue	465
Insoluble residue	250
Loss (partly organic matter)	65
Total . . .	780

The soluble residue contained chlorides and sulphates, and inasmuch as both the chlorine and the sulphuric acid had been measured in this sewage-effluent, we were able to apportion the relative amount of these salts in the soluble residue.

The soluble residue consisted of 133.5 milligrammes of chloride of sodium, and the remainder of the 465 milligrammes, viz. 331.5 grammes, consisted of sulphate of soda and sulphate of lime and sulphate of magnesia.

The insoluble residue, 250 milligrammes, consisted of carbonate of lime and carbonate of magnesia together with alumina, oxide of iron, &c. It was shown that 134 milligrammes were not carbonate of lime.

In this sewage-effluent the total carbonic had been measured and amounted to 300 milligrammes per litre. The total organic matter had also been determined by the moist combustion, and the specific gravity had also been measured.

With these data before us, an almost complete account of the composition of this sewage-effluent may be furnished, thus :—

Specific gravity, 1000.92

(which indicates that rather more than a gramme of total foreign materials must be present in a litre of the liquid).

In one litre :—

	Milligrammes.
Organic matter (by moist combustion) . .	34.0
Ammonia	10.0
Carbonic acid in combination with ammonia and free	250.0
Chloride of sodium	133.5
Sulphates of soda and lime and magnesia .	331.5
Carbonate of lime	116.0
Alumina, silica, traces of oxide of iron, &c. .	134.0
	1009.0

CHAPTER VIII.

THE UTILISATION AND PURIFICATION OF SEWAGE.

THE sewage of the early years of the century was quite different from sewage as we know it at the present time. From Chadwick's inaugural address at University College,[1] which brings vividly before our eyes the old order of things, we gather the following particulars :—

The sewers of London remained under the management of seven separate Commissions appointed by the Crown under an Act of Henry VIII., until Edwin Chadwick, who was born in the year 1800, induced Government to abolish the Commissioners.

In the year 1848 a Public Health Act was passed and a General Board of Health constituted, and Edwin Chadwick became its secretary and moving spirit. Its numerous reports were collated, when not actually written, by Edwin Chadwick.

The glaring defects in the old sanitary arrangements are thus described :—

"The main sewers were natural watercourses which, having become offensive, had been arched over. Originally streets were provided with surface channels or kennels. These received slop-water, and becoming offensive, were

[1] Vide *The Public Health Engineer*, 22nd October 1898, page 325. Chadwick Trust. Inaugural address of Osbert Chadwick, C.M.G., C.E. (chairman of the Chadwick Trust), Professor of Municipal Engineering.

replaced by underground channels of the roughest brick-work or masonry. These received and carried off slop-water and rain water from the streets. They were constructed on no regular design, no fixed principle. Excreta were collected in cesspools often beneath the floor of the house. The introduction of the water-closet, about the commencement of the century, though it abated the nuisance of the latrine itself, aggravated the evils of the cesspools by introducing a large volume of water, far exceeding in weight the actual excreta waterlogging the subsoil. The difficulty and expense of emptying the cesspool was increased. Cesspools were, therefore, connected to sewers by house-drains. The channels intended to carry off surface-water became sewers. Sewers and house-drains were constructed on no scientific principle. Their walls were rough, irregular, and porous. Naturally deposit took place in them; hand-cleansing was considered a normal incident in the history of a sewer. Irrespective of the volume of sewage to be conveyed, sewers were made large enough to admit of the passage of men to facilitate the removal of deposit, which would sooner or later choke the sewer. These defects and their evil influence on the public health are fully demonstrated by Edwin Chadwick in the various reports of the General Board of Health. The remedies for these evils are equally well set forth and established by evidence. It is shown that deposit could be removed by flushing. It was shown that by using pipes or channels of suitable diameters, sections, and materials, deposit might be avoided altogether—in short, that sewers could be 'self-cleansing.'"

"So long as sewers were elongated cesspools, their effluents

to the river or the sea caused little nuisance; the bulk of the sewage remained in them and putrified. Much of the liquid sewage soaked away into the subsoil. When improved sewers were introduced, sewage in a recognisable form made its appearance. The necessity for purification arose. Edwin Chadwick collected evidence as to the manurial value of sewage, and the possibility of purifying it by irrigation. He first brought sewage irrigation before the public."

These passages, which we quote in full without curtailment, will serve to educate our readers, and will prepare them so that they may be enabled to perceive that the popular idea of sewage derived from the experiences of the first half of the century does not represent modern sewage, as it exists in well-ordered towns at the present time. The old sewage differed essentially from the new in these two particulars: it consisted of the comparatively slightly diluted excreta, and it was putrid. The new sewage of the latter half, or third of this century, is a highly diluted liquid, and when well-made and well-ordered is not putrid at all.

The institution of sewage has, in fact, undergone development, like many another institution; and not until the century was half or two-thirds spent did sewage take on its typical character.

The only sewage with which we need much concern ourselves is sewage of the more modern kind, wherein the day's excreta have been very largely let down with water: it is only from the developed sewage system that the benefits of the sewage system are realised.

Our own personal knowledge, based upon scientific in-

vestigation of the nature of sewage, begins with the beginning of the latter third of the century. In the year 1867, one of us, in co-operation with Chapman and Miles H. Smith, invented albuminoid ammonia, and made analyses of the, at that time, highly sewage-laden stream at London Bridge. These analyses were published, and have been constantly referred to ever since as affording characteristic examples of the sewage-laden rivers. In the year 1872, one of us had an opportunity of making analyses of undiluted London sewage. A specimen of the sewage taken from the Fleet Ditch sewer in February 1872 appeared to be very concentrated sewage, the record for the free ammonia being 120 milligrammes per litre.[1]

Another specimen of London sewage taken in the same year, but *not* recorded as from the Fleet Ditch sewer, was very much weaker, yielding only 17 milligrammes of free ammonia per litre. It contained a considerable quantity of solid matter in solution and suspension, viz. 1170 milligrammes per litre. We have no record of the quantity of albuminoid ammonia in these sewages.

The earliest published analysis of raw sewage in which the complex organic nitrogenous matter was registered by means of the albuminoid ammonia was an analysis of Harrogate sewage in the year 1875.

The specimen of raw sewage in this instance was obtained by Mr. Way and one of us in the course of an investigation ordered by the Court of Chancery in 1875.

Mr. Way, as those who are acquainted with the history of official chemical investigations will know, was the chemist

[1] This shows that at that time the sewage in the Fleet Ditch sewer was only about half as dilute as sewage ought to be.

on the Rivers Pollution Commission before the appointment of Frankland as a Commissioner.

The analysis we regard as a very important one[1] for many reasons. The following is the record :—

	Parts per Million.
Free ammonia	55.00
Albuminoid ammonia	3.00
Chlorine	164.00
Total solid residue	786.00

It is, so far as we know, the earliest example of a really trustworthy measurement of the nitrogenous organic matter in an undoubtedly genuine raw sewage.

The small figure for albuminoid ammonia we have always considered as most significant: it affords an illustration of that natural tendency towards purification first proclaimed by the inventors of albuminoid ammonia, and consistently taught in our laboratory for more than a quarter of a century.

From the "Transactions of the National Association for the Promotion of Social Science" for the year 1874 we quote as follows :—

"Mr. Wanklyn (London) said that, without going into reasons, he would state the conclusion at which he had arrived, after very careful consideration, viz. that no mode of disposing of sewage existed so easy as, or attended with less immediate disadvantage than, the water-closet system. Even Dr. McAdam, who took the contrary view, and regarded the water-closet system as a great evil, admitted that sewage, properly speaking, was not the foul liquid it

[1] This analysis was first published in the fourth edition of "Water Analysis," in 1876, page 119.

was said to be. It was possible to mix excreta with so much water that they hardly gave off any gas and were perfectly innocuous. Occasionally, however, sewage ceased to be sewage, and it was to prevent this that their operations must be directed. The large size of some sewers, and, in consequence, the accumulation of solid excremental matters in the corners, was one of the chief causes of foul sewers; and he thought the difficulty it involved could easily be got over by the engineers if they tried. With regard to the final disposal of sewage, he held that the proper way would be to filter it rapidly, or apply some rapid, precipitating process, from which they could get a solid or semi-solid, which could be used as was found suitable, the remaining liquid being sent into the nearest river, where it would do no harm whatever."

From this passage it will be understood that, so long ago as the year 1874, the doctrine prevalent in our laboratory was that *properly made* sewage required no violent chemical treatment, and that storage and subsequent rapid filtration, or even mere sedimentation (as it is now called), was all that was absolutely called for in order to render the liquid fit to be discharged into rivers.

In those days, as communications from our laboratory showed, we also maintained that river-water ought to be well filtered by water companies before being supplied to the public; and, in opposition to some eminent chemists and sanitarians, we maintained that, having been well filtered, river-water became suitable for drinking, notwithstanding that it had received the liquid product from sewage-works. That foul water is capable of purification, that such purification is practicable, and likewise of common occurrence

in Nature by other means than by vaporisation and recondensation, has been taught in our laboratory ever since the commencement of our career. In the summer of the year 1876 we published records of experiments on weak solutions of various organic substances in water, showing that by simple filtration through a silicated carbon filter, the organic substance was destroyed and the water rendered exquisitely pure. The *modus operandi* of the silicated carbon we explained to be—that it caused the oxygen held in solution by the water to attack the organic substance. These experiments afforded examples of the action of oxygen-carriers, and the lessons taught by such experiments are especially applicable to the requirements of sewage purification.

Our views of the possibilities—or perhaps it would be more correct to say the practicabilities—of sewage purification have developed during the twenty-four years which have elapsed since the pronouncement at the Social Science meeting in Glasgow.

Then we had in view the bare rendering of the liquid not dangerous to the river, and we looked for the completion of the purification as an event which would come off in the river itself. Now we see the prospect of better purification as a preliminary in the sewage-works, and we have a vision of the sewage-works of the twentieth century, wherein sewage will undergo a "sea change," and whence it will flow forth as pure drinking-water.

One of the most important characteristics of sewage is the extraordinary composition of its gaseous contents. Attention was called to this peculiarity by William Allen Miller a long time ago. In the sewage-laden Thames, in the year 1859, at Woolwich, Miller found 63.05 c. c. of

dissolved gases in 1 litre of the water. The composition of this 63.05 c. c. of gas held in solution by the water of the river was found to be:—

	c. c.
Carbonic acid	48.3
Nitrogen	14.5
Oxygen	0.25
	63.05

showing extraordinary diminution of the oxygen.

Higher up the river the ratio of nitrogen to oxygen was quite different. Thus, at Kingston, Miller found in a litre of Thames water 52.7 c. c. of gases, consisting of—

	c. c.
Carbonic acid	30.3
Nitrogen	15.0
Oxygen	7.4
	52.7

As has been remarked by one of us many years ago in "Water-Analysis," undoubtedly the Thames water taken out of the river at Woolwich owes its deficiency of oxygen to the reducing action of the urea and other matters poured into the river in the form of sewage.

The points we desire to bring out are that sewage at its outfall from the sewer is absolutely, or almost absolutely, devoid of oxygen gas; and more than even that, sewage is greedy of oxygen gas, inasmuch as, on being mixed with water previously aërated to the usual extent, the whole mixture becomes oxygen-free. That sewage is devoid of oxygen gas, and that aëration is desirable, has indeed impressed itself upon many persons, not only in recent times, but many years ago. In the year 1876 a machine designed for the purpose of

aërating sewage was brought under our notice. The sewage was converted into spray in the air, and in that way aëration was aimed at. It is now years ago that Frankland resorted to "intermittent downward filtration," as he termed it, with a like object in view. And recently, under the whimsical name of the "bacteria bed," an arrangement designed partly to bring about aëration has been brought forward. None of these methods meets the real needs of the case, and there is urgent need of proper contrivances for the aëration of sewage.

The conditions of the sewage problem may be set forth as follows:—

First, inasmuch as sewage which enters the sewage-works to-day must be passed on to the river in a few days, it becomes imperative that the process of aëration must be quick. A week or ten days at most is the utmost time which is at disposal for the purpose of aëration in a modern sewage-works.

Secondly, economy of space is called for; and

Thirdly, economy of mechanical power.

We have recently devised arrangements which, we expect, will bring about almost perfect aëration with due economy of time, space, and power. We propose that the tanks or reservoirs which receive the sewage in sewage-works should, by means of a very simple contrivance, be transformed into aëraters.

The actual absorption of air takes place only at the very surface of a liquid, and the passage of the absorbed air from the superficial layer of the liquid into the body of the liquid at a distance from the surface is an exceedingly slow process. Of the exceeding slowness of this transmission

we have, in the course of our experience, had very striking exemplification in the instances of stagnant waters, which, notwithstanding many weeks' exposure to the air, exhibit a constancy of badness that is most remarkable.

In order to aërate a mass of liquid, mechanical assistance is called for, and mere agitation with wave-action is comparatively useless. The liquid mass requires that there shall be actual displacement—not wave-action, but translation. Since the surface of the liquid is aërated, the effort must be made to continually remove the aërated superficial layer and place it in contact with liquid far away from the surface.

In order to cause aëration of the whole mass of the liquid, the plan we propose consists in the continual removal of the uppermost layer of liquid, and the continual putting of that uppermost layer down to the bottom of the reservoir. We feed at the bottom and run liquid off from the top. The annexed diagrams will serve to explain the proposed arrangement (see pp. 94, 95).

The drawings will to a great extent explain themselves. Let us suppose that we had to convert a large sewage-tank or sewage-reservoir into our aërater.

For the sake of definiteness we will suppose the sewage-tank to be 100 feet in length, 25 feet broad, and 7 feet deep.

The first step would be to divide it into three compartments of 33 feet by 25 feet each, by means of two thin partitions across the tank. The pipes would have to be placed as in the drawing, the row of pipes in the first compartment opening 4 inches below the top of the tank; the row in the second compartment 8 inches below the top; and the row in the third compartment 12 inches below the top.

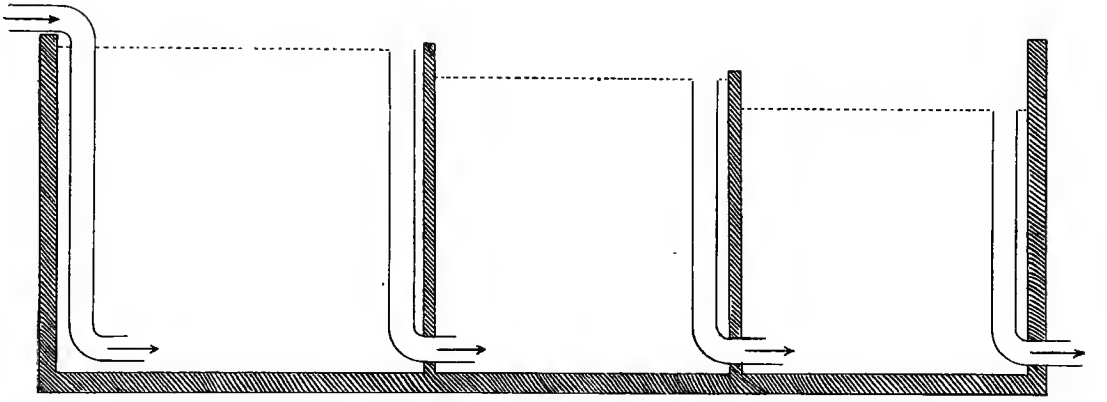

FIG. 5.—SECTION OF THE AËRATER: SIDE VIEW: DIAGRAM NOT DRAWN TO SCALE.

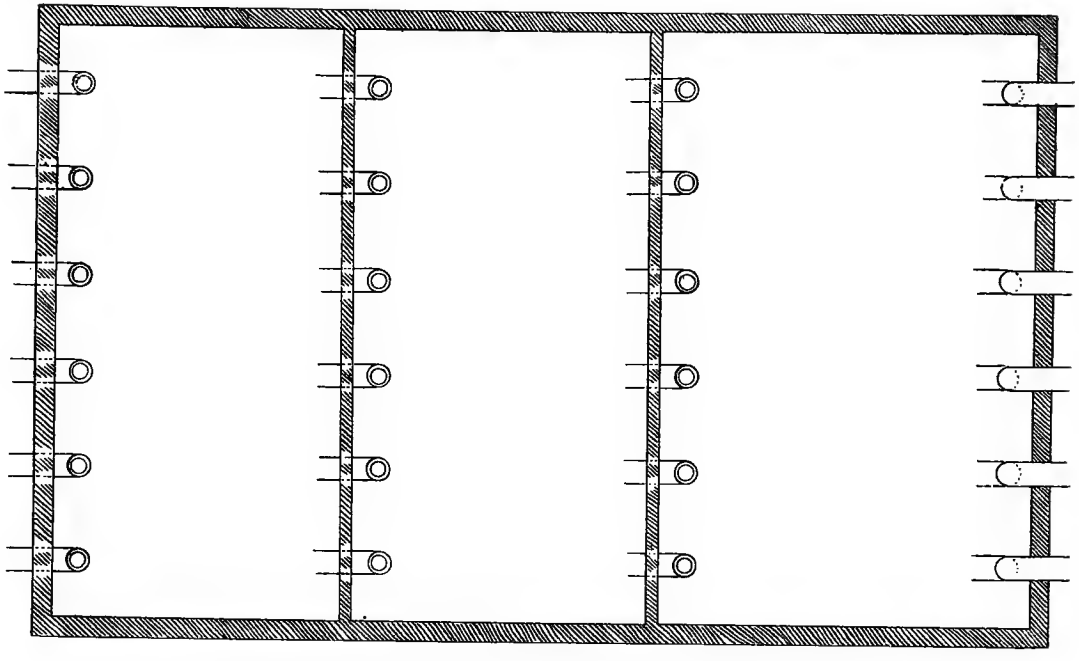

FIG. 6.—AËRATER VIEWED FROM ABOVE: DIAGRAM NOT DRAWN TO SCALE.

In working an aërater-tank of this kind, it is assumed that it is always kept fully charged with liquid, which in Compartment 1 would come up to 4 inches from the top; in Compartment 2 up to 8 inches from the top; and in Compartment 3 up to 12 inches from the top.

Assuming that the sewage was raised to the top of the tank to begin with, it will be noted that in traversing the aërater there is a fall of one foot, and that three separate aërations are thereby accomplished.

By this arrangement, with its very slow and regular current, and absence of wave-action of all kinds and steady uprising of the liquid, we should expect to insure that not a single gallon of sewage that passed through the aërater would escape being thrice exposed to the air.

The capacity of water for absorbing oxygen from the air is not great. At the very outside one litre of water could not take up so much as 10 milligrammes; and, as a matter of fact, about half that quantity is as much as would be absorbed in any reasonable time.

In order that sewage might clean itself by oxidation in the manner we are contemplating, at least six saturations would be required, and *at least two* sewage-tanks converted into aëraters in succession would be called for.

Furthermore, we require not only good aëration of the liquid, but also the action of an oxygen-carrier, so as to utilise the oxygen which has been dissolved by the liquid. One of the best oxygen-carriers is carbon in the state of charcoal (not in the state of coke); and there is a multitude of other oxygen-carriers, some of which are living beings. Here we may just mention that one of the fashionable delusions of the day is that the oxidation of organic com-

pounds demands the presence of living organisms in order that it may be accomplished. That fashionable fad of the day owes its existence to curious ignorance or obliviousness and denial of some of the oldest and best established truths of chemistry.

Reverting to the construction of the sewage-aërater, it will doubtless be observed that we have not specified either the diameter or the number of the pipes. We have drawn the partitions separating the compartments, so that each comes up a little higher than the adjacent set of pipes. What would happen if the pipes were too few or too narrow? We reply that, in that case, the level of the liquid would rise, and the liquid would run over the partitions, making little waterfalls. The remedy would, of course, be to widen the pipes and to have more of them. If the pipes were too numerous and too wide, the only evil would be waste of pipe, and there would be no hindrance to the working of the machine.

Obviously, too, instead of pipes there might be simply an additional partition attached to both sides, but not quite reaching down to the bottom of the tank; and that arrangement would be equivalent to having only one flattened-out pipe. *Vide* the drawing, fig. 7.[1]

An important item in the plan is that the fall of liquid should be very gentle, and we have drops of only 4 inches in 33 feet. Though there will always be a slow, regular current, there will likewise be deposit of sediment in such a tank. Chapman's famous experiments on filtration, published by him in the second edition of "Water-Analysis"

[1] These arrangements are protected. *Vide* Provisional Specification, No. 1934, 27th January 1899.

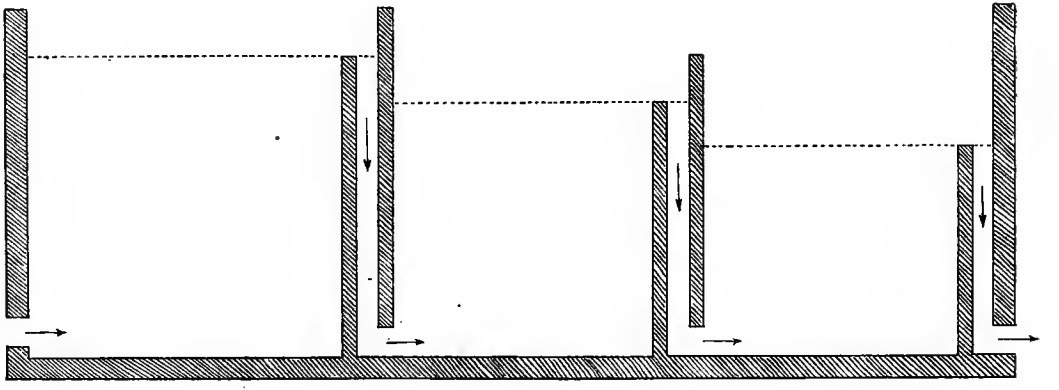

FIG. 7.

in the year 1870, guarantee that this deposit will take place in such an arrangement as we have described.

In fine, we see the sewage-works of the future as consisting of several large tanks or reservoirs which have undergone conversion into aëraters. To work the set of aëraters the sewage must be elevated, so that it has to fall about 7 feet. The first tank it will enter in the condition of typical sewage; the last tank it will leave in a cleansed condition, and will be fit to drink, and certainly fit to flow into the river.

The question of the possibility of utilising sewage was very fully dealt with more than thirty years ago, and the lapse of time has in the main confirmed the authoritative statements prominently put forward many years ago. In a paper in the *Journal of the Chemical Society* for the year 1866, by Lawes and Gilbert, the subject of utilisation is almost exhaustively treated in a manner which appeals to the judgment of most chemists.

In that paper it is very clearly set out that the constituent of sewage which has most value as manure is the ammonia, but that the extreme dilution of the ammonia which exists in sewage is a bar to utilisation in any other manner than by irrigation.

At the same time it was most conclusively shown by experimental culture, continued during several years, that by a copious application of sewage to meadow-land, the grass crop was greatly increased in quantity and also improved in quality. The volume of sewage to be applied to an acre of grass may be from one to two million gallons per annum, applied pretty evenly throughout the year. The effect of such treatment would be to increase the yield, so that the

acre should produce thirty tons of grass more than it would produce without sewage.

Under proper management, cultivation of that kind would have a fair prospect of being financially successful. The proper management includes that very little should be spent in the distribution of the sewage.

If two million gallons of sewage were applied to the land, an expenditure of so little as one penny per thousand gallons in pumping and distribution would be fatal to financial success. In order that sewage may be profitable, it must be delivered by gravitation, and in that manner distributed almost without cost.

A million gallons of typical sewage is a little less than the annual output of 100 individuals of the population.

At Croydon in the year 1866, as we learn from the paper by Lawes and Gilbert, about 250 acres were then under sewage irrigation, each acre receiving rather more than a million and a third of a million gallons of sewage in the course of the year. The Croydon sewage-farm has survived to the present day, and affords one of the most favourable examples of cultivation by the utilisation of sewage.

Apparently in the year 1866 one acre of the sewage-farm received the sewage produced by about 100 persons, or a little over 100 persons.

In the year 1888 the late Dr. Alfred Carpenter read a most interesting paper on the subject at the meeting of the British Medical Association in Glasgow.

Speaking of his experiences in Croydon, Dr. Carpenter said :—

"1. The utilisation of sewage has been carried out on the same land consecutively for thirty years, frequently in a

bungling manner, the area, however, being increased as the increase of population required it. Commencing with 36 acres only in 1851, it was all but abandoned as an incorrect proceeding because the quantity of sewage applied was in excess of the power of the soil to deal with it. Three hundred acres were then obtained about *the time that I first became connected with the farm.* These have been increased by new purchases as the quantity of sewage to be applied from increasing population rendered it absolutely necessary to enlarge the area of application, but the land irrigated for the first time thirty years ago still continues in use, and effects its object as perfectly as on the first application.

"The subsoil of the farm two feet below the surface shows very little alteration, and three feet below it is not in any way contaminated by the continued application of sewage. The various crops grown upon the land take out the manurial properties of the sewage, and allow the soil to continue its purifying power even better than at first. To effect this, however, it is necessary that the cropping be incessant, and that the land have occasional rest for a year from sewage application. The tendency of the repeated application of sewage to land is to silt up the lower portion of the subsoil and prevent it acting as a filter below the plough level, except for a short time. It follows, therefore, that the sewage must pass over the land rather than through it, and although intermittent downwards filtration may purify the water, it will be temporary only, unless the soil is turned over frequently so as to allow of its aëration. A sewage-farm will bear deep ploughing better than other land and grow larger crops in consequence.

"2. The second great fact is, that notwithstanding the very

large price paid for the land at Beddington and Norwood, namely, sometimes as much as £300 an acre, or more for some of it, and a total cost of nearly £250,000, it has seldom been necessary to make more than a twopence rate upon the parish to meet all the charges required to be met. The capital raised is now being paid off, but not lost, and in forty years from the last loan the whole farm will be the freehold of the borough, without any liability at all upon it, paying a fair sum towards the reduction of the rates, and retaining a large open space with abundance of vegetation in the midst of a large population, and providing a considerable amount of out-of-door work. The capital raised is an investment for the future, and not a scattering of immense sums of money in works which may become useless, like to those now being carried out by the Metropolitan Board of Works at the Thames outfall by Crossness and Barking."

"I showed that in 1881 the average death-rate for ten years for the Beddington and Wallington district was 14.3. I reproduce the table with additions up to the present time. The deaths have not exceeded in number those in 1881, although the population has risen very considerably. and the births are twenty more than in that year. The rateable value of the district in 1861 was £11,700, in 1871 was £20,671, and in 1881 was £41,616, and this year it is returned in the report to Surrey County Quarter Sessions as £47,424, a tangible evidence of the increase of wealth and population around the sewage-farm, whilst the zymotic death-rate last year is 0.5 only, and the average on the last seven years is only 1.2.

"As regards its effect upon the health of the borough of Croydon, I showed in 1881 that the average death-rate for

the borough was 17.9 and the zymotic death-rate was 2.79. In 1886 it was 14.5 and the zymotic death-rate 1.53. In 1887 it was 14.7 and 2.2 respectively, the dry summer increasing the diarrhœa among infants.

"I need not follow this head any further, except to remark that in February 1887 I submitted a report upon the subject to the Society of Arts in London, in which I conclusively proved that in no single instance out of nearly 100 cases in which sewage has been utilised by broad irrigation, had any fact been proved to establish the allegations of 'insanitariness' which are sometimes raised against them.

"As to the character of the effluent, it continues to be perfectly satisfactory. The analyses which are occasionally made by the local authority establish its maintenance of standard, which is very similar to that given by me to the International Congress, whilst no questions have been raised upon this point except whilst the Norwood farm was overtaxed by excess of sewage.

"Dr. Angus Smith's report to the Local Government Board in 1879 was to the effect that, as regards this form of treatment of sewage, it maintains its position, namely, 'that in every respect the best results have been obtained by irrigation.'

"The third and fourth propositions need not be further discussed, for no proof has been even tendered to the contrary except by Dr. Tidy in his communications to the Society of Arts, which were based upon suppositions made twenty years ago, not upon any solid foundations whatever, a point I was able to prove conclusively in my reply to his paper before the Society of Arts, and to which I have already referred; and even Dr. Cobbold withdrew his antagonism

before his death, because it was proved to his satisfaction that it was based upon idea only.

"The fifth proposition is an important one. It is difficult to prove a negative. I assert that disease germs are of two kinds, corresponding with active germs and resting spores, eggs hatched and growing and eggs unhatched. The hatched eggs are rapidly destroyed by the physical conditions under which they arrive at the farm; exposure to air, a lower temperature than that necessary for warm-blooded creatures, absence of pabulum and presence of injurious gases, soon destroy their life, but the resting spores (unhatched eggs) are more persistent. They certainly arrive on the farm, and it might be expected that they would do mischief; and so they do (and would) if the sewage is not immediately applied to the land. But then, if arrested, Nature comes to our rescue and destroys them by the sulphuretted hydrogen which is engendered as soon as putrefaction is rampant; but putrefaction destroys the chance of a satisfactory financial return from the use of the sewage, and it is not to be encouraged. As soon as the resting spores come in contact with the spongioles of plant life, they are taken up with avidity, and taken in as food most energetically, much as human beings take in oysters when they get the opportunity. Some classes of plants, which I have presumed to name 'carnivorous,' among which I place rye-grass, do assimilate these germs in the most rapid and satisfactory manner, so that no particle escapes their devouring power, and the effluent, as far as my observation goes, is absolutely free from their presence.

"The seventh proposition is also a most important one. A local authority buys a site and spends a large sum in erecting tanks and machinery for chemically treating sewage.

If they give up the process, the whole sum so expended is utterly lost. Not so the sums invested in the purchase of land. The capital is there, and every farthing taken from the rates is either left in the land, and raises its capital value by increasing its agricultural power, or sends into the country an additional supply of meat, milk, and vegetables, which make an actual addition to the wealth of the nation, although the locality itself may not apparently benefit by a reduction of taxation. The Corporation of Croydon have at this moment an estate of more than 700 acres purchased for sewage-farm purposes. Its agricultural value has been raised five times over since it has been so utilised; its power to employ labour correspondingly multiplied, to the advantage of the tradesmen and owners of cottage property in the borough; whilst the housewife has the choice of so much more milk and meat than would have been the case if no farm had existed. Let these conditions be established in five hundred other districts in the kingdom, including London, and pauperism will be correspondingly lessened, because so much more labour will be provided, at least 40,000 agriculturists kept on the land who are not now employed, the price of milk kept down, whilst the thousands will have it who cannot have it now, and a mass of wealth added to that belonging to the country, which ought to recommend sewage-farming to all political economists who study production and its effect upon population.

"The financial question contained in the eighth proposition is not medically interesting, but it affects us as ratepayers. I will only remark upon it, that the greater the cost, the greater the necessity of employing capital upon the land, and the greater the amount of produce raised, the greater the neces-

sity for capital to be utilised in consuming it. The Croydon Corporation blindly allow their committee to waste the produce of the farm by preventing the consumption of produce on the farm, and thus play into the hands of cowkeepers and others who are able to get it at a cheap rate. This is a monstrous perversion of common-sense, which is bearing fruit in the fact that the receipts for produce on the farm under its increased area are less in amount than they were before the new land was added to the farm; but such is one of the penalties a town has to pay for electing representatives unable to deal with these questions from a broader view than that of self-interest for the moment.

"The last proposition has reference to situation. The sooner the sewage is on the land the better chance for a good result on every point of view. If, however, the sewage has to be pumped, it increases the financial cost, and arrangements must be made for its rapid and continuous removal. If sewage is kept moving, it may travel any distance. The farm may be forty miles from the town producing it, but if so removed the town must expect to pay a larger sum for cost of transit. This may be counterbalanced by cheaper cost of land. The expense of pumping can be calculated to within a few pounds, and if the rainfall is kept out of the sewers and proper allowance made for yard, street, and roof drainage, there need be no difficulty whatever on this head. I earnestly recommend sewage-farming as applicable to all water-closet towns without exception, and feel sure that it will be far more satisfactory for the kingdom at large when it is so utilised than for it to be sent into the Thames, the Mersey, or the Clyde, to the gradual destruction of our waterways and the removal from our midst of that which will

give sinew, muscle, bone, and marrow to a people languishing for such material, and in consequence of its scarcity at home at this moment we have to import the material required for its production from the other side of the globe."

The late Dr. Carpenter was one of the most distinguished exponents of sewage-farming, and we have preferred to give his own words. The general conclusions at which he had arrived were set forth by him in the following nine propositions, which he submitted to the International Congress assembled in London in the year 1881 :—

"(1) That the application of the sewage of a water-closet town to land in close proximity to dwelling-houses is not injurious to the health of the inhabitants of those houses, provided the sewage be fresh; that it be applied in intermittent manner, and the effluent be capable of rapid removal from the irrigated fields.

"(2) The judicious application of sewage to soil of almost any kind, if it be mainly inorganic, will satisfactorily cleanse the effluent water and fit it for discharge into any ordinary stream, provided the area treated is not less than an acre for 250 persons.

"(3) That vegetable products grown upon fields irrigated by sewage are satisfactory and safe as articles of food for both animals and man.

"(4) That sewage-farms, if properly managed, do not set up either parasitic or epidemic disease among those working on the farm, or among the cattle fed upon its produce.

"(5) That this immunity exists because the conditions necessary for the propagation and continuance of those disease germs which affect man and animals are absent, the microbic life on sewage-farms being antagonistic to the life

of disease germs, the latter therefore soon cease as such to exist.

"(6) That sewage-farms may be carried on in perfect safety close to populations. It is not, however, argued that the effluent water is safe to use for dietetic purposes.

"(7) That there is an aspect in sewage-farming which shows that it is a wise policy for the nation to encourage that form of utilisation from a political economy point of view.

"(8) That to be financially successful, such farms require that the rainfall be separated from the sewage; the area large enough for alternate cropping, and the capital employed sufficient to ensure a continuous and rapid consumption of the crops produced.

"(9) That if practicable, sewage utilisation by surface irrigation should be, for financial reasons, within the area of its own watershed, and close to the populations producing the sewage; but it is not a necessity that it should be so provided it be applied to the land within a few hours—not more than twelve—of its discharge, and that there is no arrest of movement for more than very short periods before it is so utilised."

Sewage-irrigation, which, according to the account we have quoted, began in Croydon in the year 1851, has now been in operation for well-nigh half a century. Beginning with 36 acres under sewage-irrigation, the stages were 300 acres, and in the year 1888 there were 700 acres under sewage-irrigation; and the cultivation still goes on, and in all probability the farms have been still farther enlarged. The mere survival of the system for that length of time in a thriving town, the inhabitants of which double their

numbers in the space of ten years, is a most significant fact which cannot be ignored,

In his paper read before the meeting of the British Medical Association, Dr. Alfred Carpenter laid stress upon the statistical evidence of the healthiness of the district. That the sewage had undergone purification, and that the effluent from the farm has exhibited a most satisfactory degree of purity, we are able to vouch for. The following analyses of the effluents were made by ourselves in the year 1880.

Analyses of the Effluent from the Croydon Sewage-Farm.

Date 1880.		Milligrammes per Litre (or parts per Million).		
		Chlorine.	Ammonia.	
			Free.	Albuminoid.
Mar. 16	Beddington outfall . .	43.0	4.00	0.55
Mar. 26	South Norwood farm .	85.0	6.00	1.00
Aug. 19	Croydon-sewage farm .	89.0	20.00	1.00
Oct. 17	Field outfall, Beddington farm	35.7	2.00	0.44
Oct. 17	Lower farm outfall, Beddington farm . .	39.0	0.80	0.44
Dec. 12	Beddington farm, Croydon side	39.0	14.00	0.90
Dec. 12	Lower farm outfall . .	39.0	4.00	0.20
Dec. 16	New Road, Beddington, farm	29.0	6.00	0.60
Dec. 16	Lower farm outfall, Beddington	30.0	20.60	0.10
Dec. 24	South Norwood farm outfall	60.0	4.00	0.40

In two of these samples of effluent the figure for albuminoid ammonia is not so high as it is sometimes in drinking-water which contains peat. Apparently Croydon has accomplished the task of disposing of its sewage in a

manner which meets all sanitary requirements and which is at the same time a source of profit.

We have already called attention to the difference between the sewage of the beginning of the century and the sewage of the present time. The greater richness of the earlier sewage, and the irregularities in the composition of the sewage in different parts of the same system of sewage, fostered the false estimate of the strength of sewage which was current thirty-five years ago; and that false estimate is answerable for many abortive attempts to reap profit from sewage. In the excellent paper by Lawes and Gilbert, to which we have referred, there is the following table, showing the proportion of ammonia in samples of Metropolitan sewage taken from different sewers. It is a very instructive table. We have abridged the table and translated the results into the metric system.

Authority.	Name of Sewer.	Ammonia, Parts per Million.
Way . . .	Barrett's Court . . .	590
„ . . .	Dorset Square . . .	257
Letheby . .	The Fleet at noon . . .	74
„ . . .	The Fleet at midnight . .	121
„ . . .	Dowgate Dock at noon . .	143
„ . . .	Dowgate Dock at midnight .	49
Hofmann & Witt.	Savoy Street	117

"The results given at the head of the table, on the authority of Mr. Way, are those of probably the first analyses made of the Metropolitan sewage." The remark is very justly made that Mr. Way, when he published the figures, was careful to warn chemists against taking them as a measure of the value of London sewages.

The extraordinary yield of ammonia from the sewage

drawn from Barrett's Court by Mr. Way in or before the year 1863 is worthy of note for many reasons.

We have mentioned[1] that typical sewage contains 61.2 parts of free ammonia per million, and that is most probably a close approximation to the real average of the sewage in London of the present time. Mr. Way's figures for the sewage of Barrett's Court show that in that locality the dilution was not 1 part of urine to 100 parts of water, but 1 part of urine to 10 or 11 parts of water. It is highly probable that, in those days, there was much imperfectly made sewage in London.

The last figure in the table, viz. 117 parts of free ammonia in the sewage of Savoy Street, has some claims to be regarded as an average sample of the sewage of thirty-five years ago. We read the following details. "The sample analysed by Messrs. Hofmann & Witt was a mixture of equal portions taken every hour during twenty-four hours of dry weather, and there is no doubt that that sample had better claims to be taken as representing the average dry-weather sewage of the Metropolis than any other that had up to that time been collected and examined. It was upon the analysis of this sample that Messrs. Hofmann & Witt, calculating the value of the ammonia organic matter, phosphoric acid, and potassa which it contained, estimated that the constituents in one ton of such dry-weather sewage would be worth rather over twopence, and according to the information supplied to them for the purpose of their calculations, the quantity of sewage, exclusive of rainfall, would be about 158,000,000 tons per annum, or scarcely three-fifths as much as that assumed in

[1] *Vide* page 56.

the estimates of Baron Liebig and Mr, Thomas Ellis as the total sewage, viz. 266,000,000 tons. Yet Messrs. Hofmann & Witt's estimate of a little over twopence for the value of the constituents in one ton of the normal dry-weather sewage was taken by Mr. Ellis in his application for the concession of the Metropolitan sewage, as applying to the whole amount of dilute sewage (inclusive of rainfall and subsoil water), which he estimated would be available for utilisation (266,000,000 tons), and his calculations of profit to his company and to the ratepayers were based upon this erroneous assumption." This quotation will serve to bring before the minds of our readers of to-day the views of the possibilities of sewage utilisation in the year 1866. The public suffered at that date from a kind of "South Sea Bubble" in relation to sewage, and Lawes and Gilbert deserve great credit for their efforts to rid society of its delusions. Those of our readers who desire more information on this subject we would recommend to study the admirable paper which we have quoted (vide *Journal of the Chemical Society* for the year 1866, pages 80 to 128).

Since the publication of this paper, the alteration in the value of ammoniacal salts has tended to give emphasis to the criticism. To-day, ammonia, in the convenient form of sulphate of ammonia, is to be bought on the large scale at the rate of fourpence per pound of real ammonia; and the present value of the ammonia, and other substances having manurial value, existing in the solid and liquid excreta produced by *the average individual of the population in the course of a year*, may be computed as being from five to six shillings. The water-closet system causes such dilution of the excreta, that this five or six shillings' worth of ammonia

and phosphates is diffused through about 12,000 gallons of liquid, and in that manner is deprived of value, since the cost of recovery in a portable form would exceed the five or six shillings. And to-day it is now very generally admitted that, except for purposes of irrigation, sewage is absolutely worthless.

In concluding our observations on this branch of the subject, we have now to say how far we are in accord with the views so eloquently put forward by the late Dr. Alfred Carpenter. We incline to the opinion that about one million gallons of sewage per acre per annum is about as much sewage as should be applied to land; in this respect we adopt the recommendations of Lawes and Gilbert in the year 1866; and that implies that one acre would be required for the reception of the sewage of rather fewer than 100 persons.

A point which has been insisted upon, and we think with reason, is, that the enormous extent of grass-land required by the entire population of this country, if sewage irrigation were universal, constitutes a fatal objection to exclusive resort to sewage irrigation.

The five million inhabitants of London and its suburbs would require 50,000 acres of sewage-farm; and we think that it would not be profitable to devote so much valuable land to that purpose. Resort to the sewage-farm when the circumstances are favourable is desirable, and sewage-farms as adjuncts to the sewage-works will probably become the order of the day. Irrigation or the sewage-farm, as we have said, in addition to its claims as the one practicable means of utilisation, has likewise claims as a means of purifying sewage. In reference to these claims we must call

attention to the obvious clumsiness of the sewage-farm for purposes of purification.

The sewage-farm occupies from twenty to forty times as much ground as the corresponding sewage-works, computed to have tank-room for the storage of a ten days' yield of sewage, as may easily be verified by simple calculation from very obvious data. Where ground is valuable, the sewage-works would naturally be preferable to the sewage-farm, if only the sewage-works could perform a sufficiently satisfactory purification of the sewage; and the history of the treatment of sewage affords a most remarkable example in point. About the year 1871, and under the influence of that which we have likened to the old South-Sea Bubble infatuation, there came into existence the Native Guano Company with its so-called A B C plan of sewage purification. We do not think that we are wronging the parents of the Company when we say that they appear to have commenced operations under the belief that, by the A B C process, they would obtain a rich precipitate which would retain so large a proportion of the manurial constituents of the sewage as to render the collection of the precipitate an operation leading to financial benefit. At the same time that they obtained a precipitate which, when sufficiently dried, would find a market as a manure, they expected to purify the sewage so that it might be run into rivers. Thus they looked for the accomplishment of two important objects, viz., the recovery of some of the manurial value of the sewage, and the purification of the effluent. No fair-minded person, with the actual facts before him, can fail to see that a very substantial success has been achieved by this company. The manure

(native guano, it has been called) is saleable, and is really valuable. It is perfectly true that only a small fraction (probably not more than one-fifth or one-quarter) of the real manurial value of the excreta which go to form the sewage is recovered. There is also no doubt that a very decided purification of the liquid is likewise brought about.

The following analyses of samples of the effluent turned out by the Native Guano Company's works at Aylesbury were made in our laboratory some years ago.

The six samples were taken on six successive days in October 1880.

	Milligrammes per Litre (Parts per Million).			
	Total Solids.	Chlorine.	Ammonia, Free.	Ammonia, Albuminoid.
Sample 1 . .	614.00	87.00	22.00	0.76
„ 2 . .	586.00	50.00	12.10	0.60
„ 3 . .	614.00	39.00	5.30	0.36
„ 4 . .	486.00	39.00	4.10	0.32
„ 5 . .	486.00	36.00	5.00	0.20
„ 6 . .	770.00	50.00	5.00	0.40

At Aylesbury the Native Guano Company has produced effluents which were quite as good as the effluents from sewage-farms, in fact, better than that which leaves most sewage-farms.

Incidentally, and indirectly, the Native Guano Company has rendered a most important public service, the nature of which we will endeavour to explain. Every town which is supplied with water from a gathering-ground requires large reservoirs for the storage of the water, and there must be storage of a half-year's supply of water in order to avoid the risk of water-famine.

After having been used for the various purposes of daily life, the water finds its way into the drains and sewers, and ultimately issues from the sewers. By establishing and maintaining for well-nigh thirty years large works for the precipitation of matter existing in sewage, the Native Guano Company has brought in the custom of storing sewage in open tanks or reservoirs. That alone is a great achievement in sanitation, and would entitle the Native Guano Company to the gratitude of the nation.

The mixture of chemicals employed by that Company—alum, blood, and charcoal—has in times gone by provided amusement for chemists. But one of the three is unquestionably a desirable addition to sewage, viz., the charcoal, which, if properly applied, forms a most effective oxygen-carrier. The alum, or preferably the sulphate of alumina, is also useful. There is, however, a drawback to its employment where there is deficient aëration, because under those conditions it gives rise to sulphuretted hydrogen and (worse than that) to very malodorous organo-sulphur bodies.

A very important practical point in the actual working of the Native Guano Company has been that the proportion of the chemicals added to the sewage has always been very small indeed; fortunately, if the proportion had not been minute, the financial side of the Company's undertaking would have suffered. And so it has come to pass that not only has the Native Guano Company dedicated to sanitation a reservoir-capacity for several days' sewage, but having done that, it has not deprived sanitation of the boon by filling up the reservoirs with useless lumber.

In this connection it may be well to mention a scheme

of sewage purification recently put forward by the late chemist to the London County Council.

The peculiar feature of this scheme is, that it employs tanks or reservoirs in which it seeks to purify sewage, but that instead of employing small proportions of material to bring about precipitation, it more than half fills the tanks or reservoirs with non-porous, or only slightly porous materials. Into these tanks, containing coke or breeze or pebbles or fragments of burnt clay, or all of these materials, it pours the sewage after it has been strained through a sieve. Having charged the tank with sewage poured in from above, it allows it to remain at rest for two hours, and then draws the liquid out from the bottom and puts it into another tank charged either with similar materials or else with sand. These arrangements are referred to in a treatise on the subject in rather curious language as "*filter beds*," or rather "*bacteria beds*," as they are preferably called. "Suggestions for Sewage Works conducted on Biological Principles" is the heading of the chapter describing those arrangements; and elsewhere in the treatise there is the following amusing statement:—

"I pointed out in 1887 that without the intervention of living organisms no material destruction of the complex bodies existing in sewage could take place. This was the fundamental idea underlying my work in connection with the purification of the Thames."

It is hardly necessary for us to remind our readers that such substances as finely-divided sulphuret of iron in presence of air, finely-divided platinum black, finely-divided charcoal, peroxide of hydrogen, and a great multitude of other substances, some of which are found in sewage and

sewage-effluents, are capable of destroying the complex organic substances in sewage; and the statement just quoted affords a characteristic example of that curious obliviousness of the plainest and best-established chemical facts which is occasionally met with in some official quarters.

Good practical work is sometimes overlaid with nonsense; but in this case the good practical result is entirely wanting, and the final effluent from the "bacteria beds" was not satisfactory. At Sutton, where the system was in operation, there were, as the mean result of fifteen examinations, 2.40 milligrammes of albuminoid ammonia per litre of effluent.

The making of "bacteria beds" involves the sacrifice of tank-room. If the tank be half filled with non-porous solids, its capacity for sewage is reduced to half. Our advice to all persons interested in sewage purification is to beware of the bacteria bed, which at one time appeared likely to involve the corporations of some of our towns in extravagant expenditure leading to no useful result. Another of the features of the teaching in the book which we have just quoted is, that although the importance of aërating sewage is put forward, the actual arrangements of the bacteria bed are not calculated to bring about efficient aëration, but rather the contrary.

In closing this chapter we will summarise the subject of the purification of sewage as follows:—

Sewage, as it issues from the sewers, and as it is either pumped up from the sewers or as it flows from the sewers by gravitation, is dirty water containing excretal matter, partly in solution and partly in coarse and fine suspension.

In all places where the water-closet system is properly carried out, the total quantity of organic matter in the

sewage is very strictly limited. In no town with a proper water-closet system could the total organic matter in the *average* sewage exceed 300 parts per million. Half that proportion is high, and about one-third, or 100 parts per million, is probably the more usual figure.

There is a little sand and clay and other insoluble material of a mineral kind, and the greater part of the organic matter is present not in solution but in suspension.

The greater part of the organic matter is non-nitrogenous, and consists largely of cellulose and woody fibre of various kinds, and there is fatty matter.

Settlement and decantation of the supernatant liquid (which has received the convenient name of sedimentation) combined with aëration and the action of oxygen-carriers, are the processes by the aid of which sewage may be converted into comparatively clean water fit to be run into the river.

One of the most important conditions to be insisted upon is that the sewage should be allowed to remain for a sufficient number of days in the sewage-works before being (in its purified condition) discharged into the river.

A town can afford to store a half-year's drinking-water in the reservoirs of its waterworks. It would not be unreasonable to demand that the collective capacity of the tanks or reservoirs of its sewage-works should be equal to a ten days' yield of sewage, that is to say, to 330 gallons per individual of the population, and that being insisted upon, it would become quite practicable so to purify the sewage as to transform it into drinking-water.

On performing a simple calculation, it will be found that 330 gallons is equal to 52.8 cubic feet. If we take 50

cubic feet as the volume of sewage required to be stored per individual of the population, we arrive at the result that, taking an average depth of 10 feet, the ground occupied would be 5 square feet per individual. One acre is equal to 43,560 square feet. Therefore the sewage tanks covering an acre of ground would serve for a population of 8712 persons. And at that rate the requirements of greater London, with its population of five millions, would fall a little short of one square mile.

One of the characteristic advantages of our aërater is that it admits of the storage of sewage in tanks of great depth; and where land is very valuable the sewage-reservoirs might be twenty or fifty feet deep. Again, although there ought to be no hesitation in providing storage-room for ten days' sewage, if that were called for, yet we are of opinion that that is an extreme outside limit, and very likely half that amount of storage would suffice.

The ancient sewage, which Henry the Eighth's commissioners had to do with, was putrid; the modern product of a well-ordered town is not putrid.

The rational treatment of sewage consists in the promotion of oxidation, and in the avoidance of all those septic changes which involve the generation of fœtid, loathsome, and poisonous substances.

And the septic tank, and the overworked land-filter (which becomes a putrid marsh), are dangerous to the health of the community.

APPENDIX.

APPENDIX.

THE Appendix contains original papers reprinted from the *Philosophical Magazine* and the *Journal of the Chemical Society*, and from other sources. It also contains notes and explanations of various kinds, and communications from our laboratory which are here published for the first time. We have made an attempt to arrange the material in an orderly manner.

THE CHEMISTRY OF MANGANESE.

The metal manganese stands out from other metals by reason of its extraordinary acids, which have furnished the chemist with invaluable tools for the investigation of organic bodies and for some of the quantitative work in the laboratory.

The metal itself, in its metallic state, is very little known, and, so far as we know, has had no practical application of any kind. Its symbol is Mn, and its atomic weight is 55.0, its *equivalent* being 27.5.

There are *at least* two oxides, viz., MnO, manganous oxide, which is a grey-green powder forming a very *unstable* white hydrate but very stable salts; and MnO_2, which is black, and is endowed with great stability under many conditions, forming also a very stable hydrate, but with acids no stable salts.

Intermediate oxides, which most probably consist of com-

binations of these two oxides, are known. One of these, $Mn_2O_3 = MnO + MnO_2$, mixed with a little peroxide of iron and small quantities of other substances, occurs in Nature, and is called Braunite.

Another intermediate form, $Mn_3O_4 = 2MnO + MnO_2$, is known under the name of manganoso manganic oxide, and is also called red oxide of manganese. The black oxide, MnO_2, which, as we have mentioned, does not form stable compounds with acids, appears to act rather as an acid than as a base, being very apt to retain a portion of alkali forming somewhat indefinite compounds, to which the term manganites has been given.

The remarkable acids of manganese are manganic acid and permanganic acid. Apparently manganic acid exists only in its salts. The composition of the potash salt is K_2MnO_4. It is a dark blue-green solid, forming deep green solutions when treated with water.

Permanganic acid has the composition $HMnO_4$, and its potash salt, $KMnO_4$, forms beautiful crystals, opaque with a coppery lustre. The crystals dissolve in about 16 parts of cold water, yielding deep violet-red solutions.

A solution of permanganate of potash, produced by dissolving 4.00 grammes of the crystals in one litre of pure distilled water, contains one milligramme of active oxygen in one cubic centimetre of the solution, and is our *standard permanganate solution.* If the crystals of the permanganate were absolutely dry and pure, and if it were practicable to dissolve them in water without decomposition, the quantity of crystals requisite to make the solution would be 3.952 grammes of $KMnO_4$, which should be dissolved in water and then diluted exactly to the volume of one litre.

Notoriously, either on account of the impracticability of making absolutely pure $KMnO_4$, or else because slight decomposition takes place when the crystals are dissolved, therefore we do not obtain an absolutely accurate solution of the permanganate when we weigh out exactly 3.952 grammes of the crystals. Prepared in that manner the solution would be a little too weak.

We expect that the simple plan of taking a little more than the theoretical quantity, viz., 4.00 grammes, and, on the other hand, measuring out the distilled water into a well-stoppered bottle, and then putting the weighed quantity into the bottle and shaking up at intervals until the solution is accomplished, furnishes a standard oxidising solution which approximates very closely to the truth, probably better than if the exact theoretical quantity of the salt were taken. Our observations convince us that the statements so frequently made of the extreme liability of this solution to undergo change on keeping are not correct. We find that a fresh solution and a solution which has been kept for many months have almost absolutely the same strength.

We should, however, remark that our standard solution of permanganate is ten times as strong as that which many chemists have recommended; and it is not impossible that the stronger solution keeps better than a weaker one would do.

In order to work properly with this standard solution, some knowledge of the general behaviour of the compounds of manganese is desirable, and the following general statement may serve.

The permanganate performs its work by parting with some of its oxygen, which oxidises whatever may be under

examination, and at the same time gives rise to manganese-compound at a lower stage of oxidation. The distribution of the oxygen is greatly dependent upon whether the solution contains free acid or free alkali.

If there be an abundance of free acid—free sulphuric, hydrochloric, or nitric acid—and if there be *any* excess, however small that excess may be, of strong reducing agent, then the permanganate will give up its oxygen until it becomes *manganous* oxide. And in such a solution the continued existence of manganese in any other state than manganous oxide, or salts corresponding with manganous oxide, is an impossibility.

In $KMnO_4$, permanganate of potash, we have 4 atoms of oxygen, equal to 8 equivalents of oxygen. If $KMnO_4$ be subjected to full reduction in an acid solution, it loses $2\frac{1}{2}$ atoms, or 5 equivalents of oxygen, and becomes $MnO + KO_{\frac{1}{2}}$, thus:—

K	39.1	K	39.1
Mn . . .	55.0	Mn . . .	55.0
O_4 . . .	64.0	$O_{1\frac{1}{2}}$ . . .	24.0
	158.1		118.1
Oxygen given up = O . . .			40.0
			158.1

If the reducing agent be solution of the metal tin in the stannous condition, or solution of iron in the ferrous state, or dilute sulphurous acid, or hyposulphite, the action is *instantaneous;* on dropping the standard permanganate solution from the burette, each drop as it falls into the reducing liquid is *instantaneously* deprived of its colour.

So long as there is a strong reducing agent in the acid

liquid, the permanganate will continue to be destroyed and will yield manganous oxide. But the instant that the strong reducing agent is used up, another order of things will arise. The point should be carefully noted at which the instantaneous, or almost instantaneous, vanishing of the colour stops.

If the addition of the permanganate be continued after that critical point has been reached, a reverse action begins, as manganous oxide is, under the new conditions, no longer the most stable form of manganese.

When there is no excess of strong reducing agent, then, if the addition of the permanganate be persisted in, the already formed manganous oxide will come into play and become oxidised at the expense of the permanganate, and hydrated manganic oxide, MnO_2H_2O, will be precipitated in the shape of a dark brown precipitate.

The reversal of the action when the solution has ceased to be a strongly reducing medium has attracted the attention of different chemists on various occasions, but has never received quite as much attention as it deserves.

The following experiment has been recently carried out in our laboratory :—

12 c. c. of diluted sulphuric acid,
10 c. c. of oxalic acid solution,
20 c. c. of permanganate solution,

42 c. c.

were mixed together. The solutions employed were the sulphuric acid, prepared by diluting oil of vitriol with ten times its volume of water. The oxalic solution contained at the rate of 8 grammes of crystals of the acid in one litre of water, and the permanganate solution was the standard

solution, 4 grammes of $KMnO_4$ dissolved in a litre of water. As will be observed, there was abundant excess of sulphuric acid, *i.e.* between 2 and 3 grammes in the 42 c. c. of solution, whilst the quantities of the oxalic acid and permanganate of potash were equal, each being 80 milligrammes.

The liquids being kept at the ordinary temperature of the air, did not act upon one another for some minutes (oxalic acid is well known not to be so prompt in its action as stannous or ferrous solutions), but in the course of three-quarters of an hour a considerable quantity of hydrated manganic oxide was produced, and floated in the liquid, which had lost much of its purple colour. The quantities of oxalic acid and permanganate had been adjusted so that only half of the permanganate should be used up in the complete oxidation of the oxalic acid.

If there had been no *reversal* of the action, the result of this experiment would have been simply that all the oxalic acid had been resolved into carbonic acid and water, and that one-half of the permanganate had been reduced to manganous sulphate, whilst the other half had remained intact and in solution.

The production of the abundant precipitate, notwithstanding the presence of the 2 to 3 grammes of H_2OSO_3, would alone be sufficient indication of the actual course of the chemical change. We have, however, pushed our inquiry farther. The 42 c. c. was transferred to a narrow graduated cylinder and allowed to settle; a dense brown powder was deposited, leaving a clear liquid. We decanted off three-quarters of the total volume, which, instead of containing 7.5 milligrammes of active oxygen, was found to contain only 3.2 milligrammes.

At that rate, therefore, the liquid contained 4.3 milligrammes of active oxygen, and the brown precipitate contained 5.7 milligrammes of active oxygen. We washed the brown precipitate with distilled water until the decanted liquid was almost devoid of colour, and verified our conclusion by titrating the brown powder. The result of a titration of the moist precipitate was that it contained 5.8 milligrammes of active oxygen. The method employed was to dilute largely with water, and to render acid by using a little of the diluted sulphuric acid along with iodide of potassium, and finally to titrate with a standard solution of hyposulphite of soda with starch as the indicator.

Thus it is manifest that in dilute solutions containing relatively much free acid, the manganic oxide is quite as stable as the manganous oxide, unless a powerful reducing agent is also present.

Next we will consider the influence which alkalinity exerts upon the stability of the compounds of manganese.

If a solution of manganous chloride be rendered powerfully alkaline, it immediately becomes so unstable, that it cannot even be exposed to the air without absorbing oxygen and passing into the manganic oxide. The presence of strong reducing agents does not protect the manganous oxide in an alkaline liquid, and in fact the stable form in presence of alkali is the manganic oxide. Reducing agents in alkaline solution tend to reduce manganate and permanganate into the condition of manganic oxide, MnO_2.

In an alkaline solution, organic substances, in general, are attacked by manganate and permanganate at the boiling-point of water, and not even when these solutions are

boiled does the reduction of the manganate or permanganate proceed farther than the stage of manganic oxide.

Full reduction in strongly alkaline solution, brought about by the great majority of organic substances at the boiling-point of water, is thus expressed :—

$$KMnO_4 = MnO_2 + KO_{\frac{1}{2}} + O_{1\frac{1}{2}}$$

K	39.1	K	39.1
Mn	55.0	Mn	55.0
O	64.0	$O_{2\frac{1}{2}}$ . . .	40.0
	158.1		134.1
		Oxygen given up = $O_{1\frac{1}{2}}$ . . .	24.0
			158.1

In carrying out the "moist combustion" described in Chapter VI., possible modifications will suggest themselves. Instead of rendering the contents of the retort acid and then adding excess of ferrous solution and titrating back with permanganate, as has been recommended, we might titrate the excess of permanganate in the retort without first rendering the contents of the retort acid.

Péan de Saint-Gilles showed, in the year 1861, that permanganate of potash oxidises iodide of potassium into iodate of potash, thus :—

$$KI + 2KMnO_4 = KIO_3 + 2MnO_2 + K_2O.$$

By taking advantage of this reaction, it is quite possible to titrate the excess of permanganate in the retort; but we do not recommend the method.

Peroxide of hydrogen might be used, and other special reducing agents will suggest themselves.

There is, however, an objection to all these modifications, which ought to be distinctly stated. An alkaline titration

at the termination of the "moist combustion" would leave oxalates unrecorded, and oxalates are frequent products resulting from the action of strongly alkaline permanganate on organic substances.

In a strongly oxidising medium, and in presence of great excess of alkali, the most stable form is the manganate, which indeed is produced from manganese in any shape whatever when any manganese compound is fused at high temperatures with great excess of alkali and nitre or chlorate of potash. When the solid, consisting of the crude alkaline manganate, is treated with water, it gives a deep green solution, which changes in colour on exposure to the action of the atmosphere, being partially resolved into permanganate and manganic oxide by the action of the carbonic acid in the air. Apparently manganates are only capable of existing in a solution which contains a quantity of free alkali.

The change of the manganate into the permanganate and manganic oxide is expressed thus:—

$$3K_2MnO_4 = 2KMnO_4 + MnO_2 + 2K_2O,$$

and is brought about by the action of acids, and even by so weak an acid as carbonic acid.

Permanganate, which is produced from the manganate, forms a comparatively stable solution, which may be either acid or alkaline. It is in many respects one of the most potent oxidising agents known to chemists. It is at once singularly permanent and singularly active. We have made an especial study of the peculiarities of its action in strongly alkaline solution, and the records of our investigations have been published from time to time in old numbers of the *Journal of the Chemical Society* and in

the *Philosophical Magazine.* These investigations throw light on the ammonia method of water analysis and the moist combustion process. Some of the papers have been reprinted in "Water Analysis" and in "Bread Analysis." The papers which have not hitherto been republished in "Water Analysis" we now reproduce in their chronological order.

ON THE ACTION OF PERMANGANATE OF POTASH ON UREA, AMMONIA, AND ACETAMIDE IN STRONGLY ALKALINE SOLUTIONS.

By J. Alfred Wanklyn, and Arthur Gamgee.

From the *Journal of the Chemical Society* for the beginning of the year 1868.

It has been pointed out by Chapman and Smith that permanganate of potash *in presence of excess of alkali* is an oxidising agent of a most singular kind.[1]

Boiled with oxalic acid, it does not suffer any decomposition; and, as is seen in the working of the new method for the determination of albuminoid matter in waters, it may be boiled with ammonia without the occurrence of any chemical change.

The following experiments on the action of this reagent on urea, ammonia, and acetamide:—

Urea = $CONH_2NH_2$,
Ammonia = NH_3,
Acetamide = $COCH_3NH_2$,

will serve as a contribution to its chemical history.

[1] The reference to the action upon alcohol in the paper (which we omit) is not altogether confirmed by later experiments made in our laboratory. Our own unpublished results show that acetic acid is produced, but there appears to be no aldehyde.

UREA.

The urea taken for this research was prepared by the well-known process from ferrocyanide of potassium. One of the samples was proved to be pure by getting it to combine with the theoretical quantity of nitrate of mercury. Another sample was analysed by Dr. Affleck, who got from it the theoretical percentage of nitrogen by Dumas' method.

I. 0.100 gramme of urea,
1.000 „ „ permanganate of potash,
10.000 „ „ solid caustic potash,
10.000 „ „ water,

was sealed up in a tube and heated to 130° C. for twelve hours. After the experiment the contents of the tube were free from unacted-upon manganate or permanganate of potash, showing that much oxidation had taken place. On opening the tube under water, there was an escape of 15.7 c. c. of gas.

In order to ascertain whether this evolution of gas was due to the permanganate giving up oxygen, or whether it was an evolution of nitrogen from the urea, a gas analysis was made. (Frankland's apparatus was employed for this and the other gas analyses given in this paper.)

Volume taken	86
After adding hydrogen	139
After explosion	99

The gas, therefore, consisted of :—

Oxygen	15.50
Nitrogen	84.50
	100.00

Obviously, therefore, inasmuch as there was less oxygen than atmospheric air contains, the evolution of gas in our experiment was not evolution of oxygen but of nitrogen.

The space in the digestion tube unoccupied by liquid was measured, and equalled 38.1 c. c. We are thus provided with data for determining whether the permanganate had evolved oxygen, and also how much nitrogen came from the urea.

	c. c.
Volume of gas left in the tube . . .	38.1
Volume of gas escaped from the tube . .	15.7
Total volume of gas after experiment . .	53.8

consisting of 8.34 c. c. of oxygen and 45.46 c. c. of nitrogen.

Now the 38.1 c. c. of air originally present in the tube when it was sealed up contained 8.00 c. c. of oxygen and 30.1 c. c. of nitrogen.

We have therefore :—

Oxygen present originally	8.00
Oxygen found after experiment . . .	8.34

No oxygen, or only a trace of oxygen, was set free from the permanganate; also the urea had evolved about 15 c. c. of nitrogen gas.

This amount of nitrogen is not half that which the urea contained (0.100 gramme of urea contains 37.2 c. c. of nitrogen gas at 0° C. and 760 mm. pressure). A little of the nitrogen is accounted for as ammonia, for .0032 gramme of nitrogen was found in the tube after the experiment in the form of ammonia, which was distilled off and estimated by titration. Thus there remains about half of the total nitrogen to be accounted for, which must have been con-

verted into nitric acid. The circumstance that the 1 gramme of permanganate of potash had been completely reduced to the state of manganic oxide, and that there was no evolution of oxygen gas, is in itself sufficient proof that a considerable quantity of nitrogen of the urea had been oxidised to nitric acid.

In this experiment, therefore, a little less than half of the nitrogen of the urea appeared as nitrogen gas, about half was oxidised to nitric acid, and a small portion was found as ammonia.

II. In a second experiment the proportion of permanganate was increased, the object proposed being to ascertain whether greater oxidising effect would be the result of increasing the quantity of oxidising agent.

0.050 gramme of urea,
1.00 „ „ permanganate of potash,
10.00 „ „ potash,
10.00 „ „ water,

were sealed up and heated to 200° C. for four hours. After this treatment there remained much *manganate* still unreduced. On opening the tube, there was a considerable escape of gas, which was lost. Not so much as .0001 gramme of ammonia was to be found in the tube.

The experiment was repeated in order to have an opportunity of examining the gas.

0.100 gramme of urea,
2.00 „ „ permanganate of potash,
10.00 „ „ caustic potash,
12.00 „ „ water,

sealed up and heated to 160° C. for one hour. Abundance of manganate of potash remained after the experiment.

On opening under water there was an escape of gas. The total volume of gas was carefully measured, and found to be 47 c. c. at 11° C. and 744 mm. pressure, equal to 44.20 c. c. at 0° C. and 760 mm.

On analysis :—

Volume taken	160.0
After adding hydrogen	231.5
After explosion	207.5

From which is deduced :—

Oxygen	5.00
Nitrogen	95.00
	100.00

Allowing for the nitrogen originally present in the tube when it was sealed up, which may be done by taking the 5 per cent. of oxygen to be the measure of the atmospheric air, we shall arrive at the result that 33.68 c. c. at 0° C. and 760 mm. is the quantity of nitrogen furnished by the urea.

Thus we have :—0.100 gramme of urea gives 33.68 c. c. nitrogen. Theory requires that 0.100 gramme urea contains 37.2 c. c. of nitrogen.

We arrive at the startling result that by increasing the proportion of permanganate we put a stop to the oxidation. This fact, so singular at first sight, would appear to indicate that the oxidation of urea by permanganate is quick but superficial, whilst the oxidation at the expense of manganate is slower but deeper. Obviously (as will be apparent on referring to the actual quantities of permanganate and urea employed) there would still remain unattacked urea in the first experiment after the permanganate had exhausted itself

and passed into manganate. In the second experiment, on the contrary, there was enough permanganate to transform all the urea into carbonic acid, water, and nitrogen without suffering deoxidation lower than to the stage of manganate, and nitrogen once in the free state is beyond the reach of oxidising agents. * * *

Thus far we have been dealing with very concentrated solutions at temperatures considerably above the boiling-point of water. Taking weaker solutions and operating at about 100° C., we meet with a similar decomposition, only slower. The following experiment illustrates this :—We dissolved 4.75 milligrammes of urea in about 400 c. c. of pure water, added a little carbonate of soda, about 5 grammes of caustic potash, and about 0.5 gramme of permanganate of potash, and distilled for a very long time. A slow evolution of ammonia took place. Ultimately this evolution became very slow and then stopped. The quantity of ammonia obtained was estimated by the Nessler test, and amounted to 0.575 milligramme. Theory requires 2.692 milligrammes. About 22 per cent. of the nitrogen in the urea was obtained in the form of ammonia, the rest of course being either evolved as nitrogen gas or converted into nitrate. An experiment on a still smaller quantity of urea gave a very similar result. * * *

AMMONIA.

Urea being resolved into carbonic acid and ammonia by the simple assimilation of water,

$$CONH_2\,NH_2 + H_2O = CO_2 + 2\,NH_3,$$

it might be supposed that an oxidising agent applied to urea in presence of water would in effect operate on the ammonia ;

and on this ground it was necessary to study the oxidation of ammonia.

Experiment I.

0.050	gramme of	NH_4Cl,
2.00	„	permanganate of potash,
10.00	„	caustic potash,
10.00	„	water,

was heated to 150° C. for an hour and a half. Opened the tube; only minute traces of gas escaped. The gaseous contents of the tube were analysed :—

Oxygen . . .	23.00
Nitrogen . . .	77.00
	100.00

showing that the minute evolution of gas was evolution of oxygen and not of nitrogen. The residue in the tube contained only .0033 gramme of nitrogen in the form of ammonia; therefore there had been oxidation of most of the ammonia to the state of nitric acid.

In a second experiment sulphate of ammonia was substituted for the chloride of ammonium, the other things being the same and the proportion the same. The temperature was a little higher than in the first experiment. Result: no ammonia and no gas.

ACETAMIDE.

I.

0.050	gramme	acetamide,
1.00	„	permanganate of potash,
10.00	„	caustic potash,
10.00	„	water,

were sealed up and heated to 160° C. for one hour.

After the experiment there remained abundance of man-

ganate, but some peroxide of manganese had been deposited. No gas was given off, and only 0.0005 gramme of ammonia was found in the tube. The appearance of peroxide of manganese proves that reaction had taken place. Nitrates or nitrites must therefore have been formed.

The results arrived at in this paper are the following:—

Urea and great excess of permanganate in presence of much caustic potash gives all the nitrogen in the form of nitrogen gas.

Urea, with less permanganate, gives part of the nitrogen as gas and part as nitric acid.

Ammonia, whether as chloride or sulphate, is totally oxidised to nitrates when heated with great excess of permanganate and alkali. Acetamide behaves like ammonia. These reactions occur at temperatures above the boiling-point of water.

This paper, which we have reproduced almost unabridged, was read at a meeting of the Chemical Society in the autumn of the year 1867—the same year as the first publication of the "Ammonia Method of Water Analysis."

The *Journal of the Chemical Society* for the year 1868 contains, in addition to this paper, two other papers bearing on the same subject. One of these two papers is to be found in the first edition of the treatise on "Water Analysis," and the other is reprinted in the third and all later editions of that book. About the year 1871 communication between our laboratory and the Chemical Society was broken off. One of us, who was in office on the Council of the Chemical Society in the year 1867, retired from the Society about the

year 1871, and since that date nothing of ours has appeared in the *Journal of the Chemical Society* except in the form of abstracts from other journals.

In May 1877 a paper by ourselves was published in the *Philosophical Magazine*, giving many examples of the yield of albuminoid ammonia by vegetable substances. The paper was republished *in extenso* in our treatise on "Bread Analysis." It gives a fair example of the uses to which the ammonia method may be put. We reproduce it :—

"The physiological doctrine that the animal does not produce proteine compounds, but simply transforms those proteine substances which it has taken in as food, lends great importance to the determination of the amount of proteine compounds in different kinds of vegetable food; and such a determination becomes of the utmost importance both to the physiologist and from a practical point of view.

"Hitherto, however, this desideratum has been very imperfectly supplied, and the chemist has very inadequately answered the question as to the proteine value of the different vegetable foods. Gluten, legumen, vegetable caseine, vegetable albumen, as the various proteine substances occurring in vegetables have been called, vary much in properties. Some of them are soluble and others are insoluble in water, and some of them are soluble in alcohol, and it would be difficult to draw up any general method of extracting the proteine compound in a state of purity. Resort has therefore been had to elementary analysis, and chemists have deduced the amount of proteine compounds from the percentage of nitrogen found on submitting the food to ultimate analysis.

"To this procedure there are several objections, which have

apparently not been sufficiently insisted upon. Taking the case of wheaten flour (which is much more favourable than many other cases), the percentage of nitrogen is about 2.00, yet neither the Will-and-Varrentrapp process nor the Dumas process of nitrogen determination, as it is generally carried out, is at all adequate to the valuation of the proteine substance in flour.

"The Will-and-Varrentrapp process, as those who have a critical knowledge of it are aware, is subject to special failure when it is applied to proteine substances, and is not a determination of nitrogen in those instances.

"The Dumas method, as usually practised, is uncertain when it is applied to determine a minute quantity of nitrogenous substance in presence of a large quantity of non-nitrogenous organic matter. Possibly, if carried out with extraordinary care and extraordinary precautions, the Dumas process might become available for the object in view, but those persons who have practical knowledge of the difficulties besetting this particular case will admit that extraordinary care would be required, and that the process would be too impracticable for general employment.

"The method by which we seek to accomplish the task before us is, we believe, specially adapted for this description of work.

"We propose to measure the amount of proteine substances in vegetables by the amount of ammonia which the vegetables *generate* when they are subjected to the action of a boiling solution of potash and permanganate of potash; in fact, we have made a special adaptation of the well-known ammonia process of water analysis to the case of vegetable proteine.

"The working details of our process are as follows:—

"Into a litre flask a carefully-weighed gramme of the vegetable substance to be analysed is placed, and 20 c. c. of normal solution of caustic of potash[1] is added, and then water is added until the litre-mark is reached by the level of the liquid. The contents of the flask are then shaken up so as to insure thorough mixture. In this manner we obtain a liquid of such a strength that each cubic centimetre contains one milligramme of the flour or other vegetable substance to be operated upon. 10 or 20 c. c. of this liquid (*i.e.* 10 or 20 milligrammes of the vegetable substance) are convenient quantities to work with.

"The next step is to get the retort in order as for a water analysis, and to place in it 300 or 500 c. c. of good drinking-water, and to add 50 c. c. of a solution containing 10 grammes of potash and 0.4 gramme of permanganate of potash (such as is used in water analysis), and to distil until the residue in the retort no longer yields the slightest trace of ammonia. That having been done, 10 or 20 c. c. of the liquid containing the vegetable substance are to be added and the distillation proceeded with. The vegetable substance will then be attacked, and its proteine will yield ammonia, which will distil over, and may be measured by means of the Nessler test. For further details of the manner of carrying out work of this description we would refer to the treatise on 'Water Analysis,' which is now sufficiently well known to chemists.

"It was shown some years ago that egg-albumen yields about one-tenth of its weight of ammonia when submitted to

[1] Solution of potash made by dissolving 5 grammes of solid sticks of potash in 100 cubic centimetres of water will answer.

such a process as the above, and that solutions containing different quantities of egg-albumen yield ammonia exactly proportional in amount to the strength of the solutions of albumen.

"As will be observed, our present experiments include many descriptions of wheaten flour, also pea-, rice-, maize-flour, oats, barley, malt, rye, and arrowroot. The last named is important, as showing a very small proportion of proteine.

"The-pea flour was ground from the peas in our own laboratory, and passed through a very fine sieve. The rice-flour was likewise of home manufacture; and the same is true of maize and the malt. The rest were not powdered in the laboratory.

"From sixteen samples of wheaten flour we obtained:—

Name of Sample.	Percentage of Ammonia.
1. Cambridgeshire extra-superfine	1.10
2. Another sample	1.00
3. Household flour, Waterloo Bridge	1.13
4. Country flour	1.08
5. Huntingdonshire	1.05
6. Suffolk	1.00
7. Hungarian	1.10
8. Another Hungarian	1.05
9. „ „	1.07
10. Darblay, Paris	1.05
11. Vienna	1.08
12. Australian	0.92
13. Californian	1.13
14. American	1.14
15. Another American	1.17
16. „ „	1.09

"From the other nitrogenous substances we obtained :—

Name of Sample.	Percentage of Ammonia.
Pea-flour	2.30
Rice	0.62
Maize	1.03
Oats	1.00
Barley	1.10
Malt	0.50
Rye	1.45
Arrowroot	0.08

"In looking through these tables, the reader will be struck with the constancy of the quantity of proteine substances in wheaten flour. If one of the American samples (No. 15) be excluded (possibly there was a little pea-flour in that sample), it will be seen that the highest percentage of ammonia given by any sample of flour is 1.14; and excluding the solitary sample of Australian flour, the lowest yield of ammonia is 1.00. Wheaten flour would therefore seem to yield between 1.00 and 1.13 per cent. of its weight of ammonia when subjected to the above process.

"Maize, oats, and barley, as will be seen, very closely resemble wheaten flour in yield of albuminoid ammonia. Rye, on the other hand, is exceptionally rich in proteine; apparently it is the most nitrogenous cereal.

"The high percentage of ammonia from pea-flour will attract attention. The proteine in rice amounts to about half as much as in wheaten flour."

WATER ANALYSIS: DETERMINATION OF CELLULOSE AND MODIFIED CELLULOSE IN DRINKING-WATER.

By J. A. Wanklyn and W. J. Cooper.

From the *Philosophical Magazine*, June 1878.

The ammonia process of water analysis provides an index to the nitrogenous organic matter in drinking-water; but it does not deal with the non-nitrogenous organic matter, and some method whereby the non-nitrogenous organic matter might be reached is still a desideratum. This desideratum the Frankland and Armstrong combustion process aims at supplying, but (as is now pretty well understood among chemists) fails to supply. The old permanganate process, which we owe to Forchhammer, which notoriously failed in practice, would accomplish the object in view if the practical difficulties which beset it could be overcome.

If the quantity of oxygen required to oxidise cellulose or sugar be calculated, it will be seen that rather more than its own weight of oxygen is consumed by a given weight of cellulose or sugar. The estimation therefore of cellulose or sugar by means of the oxygen consumed in burning down to carbonic acid and water would rank along with the more advantageous operations of analytical chemistry.

Forchhammer's process, as hitherto practised, does not effect anything approximating to complete oxidation down to carbonic acid and water, as was illustrated by some experiments published by Frankland and Armstrong in

1868 (vide *Chem. Soc. Journ.*, vol. vi. p. 82), which we quote :—

Name of substance (30 parts dissolved in 1,000,000 parts of water).	Oxygen absorbed during six hours.	Oxygen required for complete oxidation.
Gum-arabic . . .	0.35	35·5
Cane-sugar . . .	0.15	33·7
Starch	0.30	33·5

showing that, as usually carried out, the oxidising process does not avail to accomplish more than about one-hundredth part of the task set before it. The manner in which the permanganate of potash is applied to drinking-water in Forchhammer's process is by simply mixing measured volumes of the permanganate solution with a known volume of the water to be operated upon, and observing how many volumes are decolorised by the action of the organic matter. A quantity of acid is usually added to the water, and some length of time allowed to elapse before making the final readings.

The modifications whereby we have completely altered the character of the Forchhammer process are as follows :—

Instead of simply mixing the standard solution of permanganate with the water to be examined, we distil a given volume of the water (say 1 litre) with a considerable excess of standard solution of permanganate, and thereby get more oxidising action than in the ordinary operation. We find advantage in having the liquid strongly alkaline during the distillation, but we render acid before titrating the residue.

The following are the working details :—

A standard solution of permanganate of potash (strength 0.4 milligramme of active oxygen per 1 c. c.) is prepared.

A standard reducing solution containing proto-sulphate of

iron, and of such a strength that each cubic centimetre exactly corresponds to the permanganate solution, is also prepared.

Solution of caustic potash, 5 per cent., is prepared.

Diluted sulphuric acid (1 volume of oil of vitriol with 9 volumes of water) is prepared.

These solutions being got into order, the operator may begin.

A litre of the water to be examined is placed in a retort which is conveniently mounted, just as in the ordinary course of water analysis by the ammonia process. Into the retort the operator drops with a graduated pipette 5 c. c. of the solution of potash (to render the water alkaline), and then 5 c. c. of very carefully measured standard solution of permanganate; and then the contents of the retort are boiled by means of a large Bunsen burner, and the water is rapidly distilled off. After the distillation has advanced, it will very often happen that the permanganate will show signs of having been used up; if that happens, a second and, if necessary, a third 5 c. c. of standard permanganate must be dropped into the retort, and the distillation continued until 800 or 900 c. c. have distilled over, and only some 200 or 100 c. c. of the liquid remain behind in the retort. When the distillation is stopped, the observation that the contents of the retort still contain unacted-upon permanganate must hold good; otherwise too little permanganate would have been employed in the operation.

The manner of finishing the operation is of a very obvious description. The operator acidifies the residue in the retort (*i.e.* he adds 10 c. c. of the dilute sulphuric acid); then he adds a measured quantity of iron solution, taking care to

use a considerable excess; and finally, he titrates back with the standard permanganate, and thus becomes provided with numerical data expressing how much oxygen has been used up by the litre of water.

We have just directed that 1 litre of water should be taken for an operation, and that quantity will be found convenient; but, as will strike the chemical reader who reflects on the conditions which limit the accuracy of analytical processes, there is nothing to forbid résort to a much larger scale if the highest degree of delicacy and accuracy were desired. In such a case, 10 litres successively introduced into the same retort would be advantageous.

We have worked on 4 litres successively introduced.

On applying the process we have obtained the following results:—

	Oxygen consumed per litre of water.
Excellent distilled water . . .	0.13 milligramme.
Thames water by a Water Company .	2.30 „

which show a striking difference between common drinking-water and water of the purest description.

Experiments on dilute solutions of cane-sugar have given results approximating very well to theory. Cane-sugar, indeed, we have subjected to a course of oxidations ranging over a very varied scale—from 5 milligrammes to upwards of 10 grammes at a single operation.

The reaction is precise, viz.:—

(1.) $C_{12}H_{22}O_{11}+O_{20}=11(H_2O)+4(CO_2)+4(C_2O_3)$.
(2.) $C_{12}H_{22}O_{11}+O_{24}=11(H_2O)+12(CO_2)$.

Equation (1.) is valid if the action be restricted to the alkaline solution; and equation (2.) is valid when the oxida-

tion has been carried forward so as to be finished in the acid liquid.

We postpone the publication of the experiment, and content ourselves with the general statement, that we can, by means of solution of permanganate, effect perfect combustions of a number of organic compounds, the combustions taking place whilst the organic matter remains in aqueous solution.

ACTION OF ALKALINE SOLUTIONS OF PERMANGANATE OF POTASH ON CERTAIN GASES.

By J. A. Wanklyn and W. J. Cooper.

From the *Philosophical Magazine*, October 1878.

In continuation of our work on the oxidising power of strongly alkaline solutions of permanganate of potash, we have made experiments on the common gases, and have arrived at results of some interest. The solution which we have employed in these experiments contained 16 grammes of permanganate of potash and 5 grammes of caustic potash, dissolved in a litre of distilled water.

Binoxide of Nitrogen, NO.

The gas was prepared in the usual manner by the action of diluted nitric acid on metallic copper. On submitting it to the above described solution of alkaline permanganate, there was immediate action, the gas being instantly absorbed at ordinary temperatures, and the solution being instantly decolourised and caused to deposit the brown hydrated binoxide of manganese.

110 c. c. of NO and 30 c. c. of the potash and permanganate solution were shaken up together. Immediately the solution lost its colour and deposited the brown binoxide of manganese, and 85 c. c. of the gas was absorbed.

The reaction is—

$$NO + KMnO_4 = MnO_2 + KNO_3$$

Protoxide of Nitrogen, N_2O.

This gas, prepared in the usual way from nitrate of ammonia, appears to be quite without action on the alkaline solution of permanganate of potash. Even on prolonged heating of the materials in the water-bath there was no sign whatever of action, the permanganate preserving its brilliancy and the volume of the enclosed gas undergoing no diminution.

Nitrogen Gas.

Experiments published some years ago by one of us show that this gas is not attacked by the alkaline solution of permanganate even when the temperature is considerably raised.

Carbonic Oxide, CO.

This gas, prepared by the action of excess of sulphuric acid on ferro-cyanide of potassium, is attacked by the alkaline solution of permanganate. The action is not instantaneous, as in the case of binoxide of nitrogen, but is comparatively slow.

118 c. c. of CO and 30 c. c. of the above solution of potash and permanganate of potash were sealed up and heated in the water-bath, being frequently taken out of the bath, cooled, and shaken. Altogether the heating

occupied some three or four hours. On opening the tube under water, it was found that great absorption of gas had taken place.

Of the 118 c. c. of CO taken for experiment—

92 c. c. were absorbed.
26 „ residue.

118

This action appears to be—

$$CO + O = CO_2,$$

regard being had to the amount of $KMnO_4$ which had been reduced during the operation. At ordinary temperatures the action takes place but very slowly.

Hydrogen

is also absorbed by the alkaline solution of permanganate. In an experiment in which 64 c. c. of hydrogen were sealed up with 16 c. c. of alkaline permanganate, and heated for some hours in the water-bath. An absorption of 34 c. c. of hydrogen was noted.

We are continuing the investigation.

THE MOIST COMBUSTION PROCESS: SOME REACTIONS OF ALKALINE PERMANGANATE OF POTASH.

By J. Alfred Wanklyn and W. J. Cooper.

From the *Philosophical Magazine*, February 1879.

Following up our investigations (the results of which were communicated in the June number of this Journal, and in the Chemical Section of the British Association at the

Dublin Meeting last year) we have now to announce that we have overcome one of the difficulties which stood in the way of giving to our process absolute generality of application to all organic substances.

It will be remembered that, starting with the organic substance in aqueous solution, we showed that permanganate of potash and excess of alkali burned down the organic substance to the state of carbonates, oxalates, and water; and we proposed to render the solution acid, and so, as was well known, would burn down the oxalates to carbonates. At the Dublin Meeting we announced, that although this answers very well in many cases, yet in certain classes of cases acetates appeared among the products of oxidation, and when once produced, acetates resisted further oxidation.

We have now managed to oxidise the acetates by the simple process of using considerable excess of permanganate and raising the temperature some 60 or 80 degrees above the boiling-point of water. Under these conditions acetate of potash yields carbonate of potash and apparently no oxalate whatever.

There is a difficulty, however, attendant on the use of these high temperatures; and on this occasion we wish to explain this difficulty and how it has been overcome.

The difficulty arises from the fact that at temperatures very little above 100° C. a mixture of pure permanganate of potash and caustic potash evolves oxygen gas. This fact we have very carefully ascertained both by noting the diminution in oxidising power which the solution shows after being heated to 180° in the oil-bath and by actually collecting and measuring the oxygen gas which was evolved during

the heating in the oil-bath. The gas is evolved very freely at temperatures even below 140° C.; and the numerical results accord very fairly with this equation:—

$$2(KMnO_4)+2KHO=2(K_2MnO_4)+H_2O+O.$$

Here, as will be observed, the permanganate of potash is represented as losing one-fifth of its active oxygen and yielding manganate of potash.

It has long been known that at very elevated temperatures —at temperatures bordering on low redness, permanganate of potash parts with oxygen and forms manganate of potash, that, in point of fact, at these elevated temperatures manganate, and not permanganate is the stable form of combination; but we believe this easy evolution of oxygen at temperatures a little above the boiling-point of water is quite a novelty. For the moist combustion process it would be a very uncomfortable novelty if we were unable to stop the evolution of the gas by a convenient device, since the alkaline permanganate would cease to keep a trustworthy record of the consumption of oxygen during the process.

We have, however, to add that we can stop the evolution in a most convenient manner. We mix some hydrated binoxide of manganese with the permanganate and alkali, and then there is no evolution of oxygen. Why this addition should be effective is obvious; and the chemist will have no difficulty in understanding that the necessity of having to make such a condition does not damage our process.

We have to record as an interesting reaction the behaviour of green oxide of chromium with strongly alkaline solution of permanganate of potash. It acts very readily and yields chromate of potash and hydrated binoxide of manganese;

this takes place at temperatures even below the boiling-point of water. We are following up this experiment, and hope to make new and rare metallic acids.

PRODUCTS OF THE OXIDATION OF WOOL—CYANO-PROPIONIC ACID.

By J. Alfred Wanklyn and W. J. Cooper.

From the *Philosophical Magazine*, May 1879.

In the course of the investigations which have led up to the moist combustion process, we have come across some results which appear to be worth recording. On the present occasion we single out the oxidation of wool, so as to produce large quantities of a new nitrogenous acid endowed with great stability.

When wool dissolved in water by the aid of about three times its weight of caustic potash is oxidised by four times its weight of permanganate of potash, there are produced carbonic acid, oxalic acid, and a certain quantity of ammonia; and when the oxidation is limited by the employment of only four times as much permanganate as wool, at least two new acids survive, one of which (viz., cyano-propionic acid) we have succeeded in obtaining in a state of purity.

The acids arising from oxidation under these conditions are met with in combination with potash, and mixed with the excess of caustic potash, and the carbonate and oxalate

of potash arising from the oxidation of the wool. The alkaline liquid is first filtered from the brown oxide of manganese resulting from the destruction of the permanganate, and then it is neutralised with sulphuric acid and evaporated down to crystallization. After the deposit of the greater part of the sulphate of potash, the mother-liquor contains oxalate of potash, which may be precipitated by the addition of weak alcohol; and after the separation of the oxalate of potash the alcoholic mother-liquor will be found to contain the potash salts of at least two new organic acids. One of these new salts is very soluble in weak alcohol of 40 or 50 per cent., but almost insoluble in alcohol of 84 per cent.; and this salt, which is cyano-propionate of potash, we have investigated.

In our first attempts we endeavoured to take advantage of this character in order to purify the salt; but we afterwards found that the baryta salt admits of a more satisfactory mode of treatment, and have accordingly resorted to the baryta salt.

We proceed to describe our experiment:—A large Berlin porcelain dish, capacity from 5 to 6 litres, was fitted into a water-bath and heated to 100° C. One litre of water, 300 grammes of solid potash, and 100 grammes of Berlin wool were next placed in the dish, and heated and stirred until the wool had completely dissolved in the alkaline liquid; then 400 grammes of crystals of $KMnO_4$ were gradually added. The action was energetic: ammonia was evolved; brown hydrated binoxide of manganese was precipitated, and in a short time the colour of the permanganate had completely disappeared. The whole was then allowed to settle, and partly by decantation, and partly by filtration,

the alkaline liquid was separated from the brown oxide of manganese.

The alkaline liquid was nearly neutralised with sulphuric acid and evaporated until crops of sulphate of potash separated. Care was taken to wash each crop of sulphate of potash with repeated small quantities of water, so as to avoid loss of soluble product; and the mother-liquor was mixed with a little alcohol, which threw down a quantity of oxalate of potash.

Finally, about 500 c. c. of solution containing the new salts dissolved in alcohol of 50 or 60 per cent. was obtained. This solution was evaporated down to a syrup; and at this stage the exchange of barium for potassium was managed as follows:—To the syrup 20 grammes of H_2OSO_3, previously diluted with about an equal volume of water, was added so as to decompose the potash salt. The resulting sulphate of potash was separated from the new acid by means of 500 c. c. of 84 per cent. alcohol, which dissolved the new acid and left behind the sulphate of potash. The alcoholic solution was mixed with 30 grammes of baryta which had been slaked, a little more baryta being added so as to render the liquid alkaline. The alcohol was evaporated off, and the resulting baryta salt dried up in the water-bath. After this evaporation to dryness the baryta salt was re-dissolved in water and the solution filtered and mixed with its own volume of 84 per cent. alcohol. By this treatment a white powdery precipitate of baryta salt was obtained. The precipitate was washed with 40 per cent. alcohol and afterwards pressed for some days between folds of bibulous paper.

The weight of the pressed baryta salt which retained

alcohol and water was 85 grammes, containing 25.1 grammes of baryta salt absolutely dry at 100° C.

One of the objects of this precipitation by means of an equal volume of 84 per cent. alcohol (which is equivalent to the use of 40 per cent. alcohol) is the removal of a new baryta salt which is very soluble in alcohol.

The 85 grammes of pressed baryta salt containing 25.1 grammes of baryta salt, formula $(C_4H_4NBaO_2)_23H_2O$, are the material from which we have prepared the acid and the set of salts about to be described.

In addition to the 25.1 grammes of baryta salt, there were 4 grammes of baryta salt in the alcohol employed for washing the precipitate. The yield of cyano-propionate of baryta by 100 grammes of wool was therefore 29.1 grammes; and, as will be seen on turning to the analysis, the carbon contained by the salt is 7.2 grammes.

The Berlin wool employed in these experiments had been previously examined, and a combustion of it had been made in the ordinary hygrometric condition in which it was employed: 100 grammes of the wool contain 43.40 grammes of carbon. We have likewise made quantitative determination of the carbonic acid and the oxalic acid given by the action of four parts of permanganate of potash on one part of wool dissolved in potash; also we have determined the oxygen consumed in the oxidation. The details of the experiment we will publish shortly; and likewise we reserve our commentary on the bearing of these results on our views as to the structure of horn and albumen.

Here we give the numerical results:—

100 grammes of wool (containing 43.4 grammes of carbon), when submitted to oxidation by means of four times its weight

of permanganate of potash acting at 100° C. in alkaline solution, gave—

	Grammes
Carbon in the form of CO_2	5.9
„ „ „ $C_2H_2O_4$ . . .	12.2
„ „ „ $C_4H_5NO_2$ . . .	7.2
Carbon in other forms (mostly as forming acids with potash salts very soluble in strong alcohol)	18.1
	43.4

Oxygen consumed 60.7 grms.

Cyano-propionic Acid $(C_4H_5NO_2)_23H_2O$.—This acid is prepared by decomposing the baryta salt with the theoretical quantity of dilute sulphuric acid necessary to saturate the barium, separating the sulphate of baryta by filtration, and evaporating the solution of the acid to dryness in the water-bath. The solid residue, which was carefully dried in the water-bath, has the following formula :—

$$(C_4H_5NO_2)_23H_2O.$$

We took 16.0 grammes of the moderately but not excessively dry baryta salt (the purity of which had been ascertained by a complete analysis of the sample), added 75.0 c. c. of normal sulphuric acid (3.675 grammes of H_2OSO_3), and obtained 8.773 grammes of washed and ignited Ba_2OSO_3, and 9.7 grammes of the organic acid dried in a platinum dish at 100° C.

The equation expressing the reaction is :—

$$(C_4H_4BaNO_2)_23H_2O + H_2OSO_3 = Ba_2OSO_3 + (C_4H_5NO_2)_23H_2O ;$$

and the following is a comparison between the quantities required by the equation and those given by experiment :—

	Theory. Grammes.	Experiment. Grammes.
$(C_4H_4BaNO_2)_23H_23H_2O$ . .	14.51	16.000
H_2OSO_3 . . .	3.675	3.675
Ba_2OSO_3 . . .	8.737	8.773
$(C_4H_5NO_2)_23H_2O$ . . .	9.45	9.7

The correspondence between the sulphuric acid, sulphate of baryta, and final organic acid will be noted. The want of accordance between the quantity of baryta salts taken and the quantity required by the equation, as will be understood, means that the salt was not in a state of absolute dryness. The correctness of the interpretation was borne out by the observation that on ignition the acid left no appreciable fixed residue, viz., 0.774 gramme of the solid acid left on careful ignition 0.002 gramme of ash. The acid was also ascertained to be free from sulphuric acid.

Properties of Cyano-propionic Acid.—It is an amorphous solid, brittle at ordinary temperatures, but easily softening on being heated to 100° C. Its colour is pale brownish-yellow or straw-colour; in powder it is almost white.

It is very soluble in water and in strong alchohol. Its aqueous solution is powerfully acid both to the taste and to litmus. It drives out carbonic acid from carbonates and neutralises bases completely. The specific gravity of an aqueous solution of the acid containing 15.12 per cent. of $(C_4H_5NO_2)_23H_2O$ is 1.06 at ordinary temperatures. An aqueous solution of one-tenth of this strength, viz., containing 1.512 per cent., forms a lather on being shaken up, is pleasantly acid to the taste, and is capable of dissolving metallic magnesium in the cold. In presence of metallic mercury the action of the magnesium is brisk;

and in the space of twenty-four hours, 10 c. c. of the weak acid liquid confined over mercury had evolved almost the theoretical quantity of hydrogen which the magnesium was capable of displacing.

Cyano-propionic acid is attacked when it is sealed up in a tube with the acid 8 per cent. bichromate solution and heated to 100° C. Under these conditions very little oxygen is taken up and carbonic acid is formed in considerable quantities. In alkaline solution, when boiled with permanganate of potash, it is slowly attacked, and takes up one-third of its weight of oxygen. When heated to about 200° C. with great excess of potash, it suffers a very interesting decomposition, which we are at present investigating.

When the acid is heated above 100° C. it loses weight and becomes constant at about 140° C. After repeated heating to that temperature, the formula of the acid (judging by the loss of weight) appears to be $C_4H_5NO_2$. At temperatures above 140° C. the acid continues to lose in weight, but apparently undergoes decomposition, inasmuch as it evolves a very peculiar smell, reminding us of cyanide of ethyl. A portion of the acid which had been dried at 140° C. lost about half of its weight when heated to 220° C., and yielded a brown or black mass insoluble in ether and water, but soluble in caustic potash. On ignition a small quantity of charcoal difficult of combustion remains. The proportion of such charcoal yielded by the acid dry at 140° C. is about one-sixth of the weight of the acid. On continuing the application of heat, this charcoal gradually burns away, and no residue is left.

As will be seen presently, most of the salts of cyano-

propionic acid are soluble in water; the only exceptions we have met with being the salts of silver, lead, and peroxide of iron. Solutions of cyano-propionates give no precipitate with salts of alumina, copper, and peroxide of mercury. Those cyano-propionates which are soluble in water are insoluble, or very sparingly soluble, in strong alcohol. Certain salts, as, for instance, those of lime, baryta, and magnesia, are very sparingly soluble even in 40 per cent. alcohol.

As a rule, the salts of this acid exist in combination with water. The only salt which we have found to be nearly anhydrous is the silver salt. So far as we have ascertained, decomposition sets in before the hydrated salts give up the last portions of water.

Cyano-propionate of Baryta, $(C_4H_4NBaO_2)_2 3H_2O$, is obtained in a state of purity, as has already been described, by precipitating its strong aqueous solution by means of an equal volume of 84 per cent. alcohol. The precipitate is a powder almost absolutely white, which may be washed with 40 per cent. alcohol, in which it is very sparingly soluble. It should be afterwards pressed between folds of bibulous paper and dried in the water-bath. After prolonged drying at 100° C. it has the above formula, and has furnished the following results on analysis:—

I. 0.923 gramme burnt with chromate of lead, copper turnings being used in front of the combustion-tube, gave 0.290 gramme of water and 0.842 gramme of carbonic acid.

II. 1.471 gramme gave 0.907 gramme of sulphate of baryta.

III. 0.259 gramme gave 0.157 gramme of sulphate of baryta.

IV. 0.958 gramme gave 0.587 gramme of sulphate of baryta.

V. 0.398 gramme burnt with CuO and copper turnings gave 20.61 c. c. of nitrogen gas at 0° C., and 760 mm. nitrogen per cent. = 6.51.

$(C_4H_4NBaO_2)_23H_2O$.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
C_8 . . .	96	24.81	24.88	...	...	...	...
H_{14} . . .	14	3.62	3.49	...	...	...	...
N_2 . . .	28	7.23	...	...	...	...	6.51
Ba_2 . . .	137	35.40	...	36.26	36.03	35.64	...
O_7 . . .	112	28.94	...	...	...	...	...
	387	100.00					

At 160° C. to 170° C. the salt loses one atom of water, becoming $(C_4H_4BaNO)_22H_2O$, but regains the water on exposure to the atmosphere at ordinary temperatures and under ordinary conditions.

It is very soluble in water, and only sparingly soluble in 40 per cent. alcohol; the degree of solubility being about one part of the salt to one hundred parts of the alcohol of that strength.

There is a basic baryta salt which is obtained by adding baryta-water to the solution of the neutral salt, and then precipitating by the addition of an equal volume of 84 per cent. alcohol. The salt forms a white precipitate, which, after drying at 115° C., contained 42.84 per cent. of barium. The theory for $(C_4H_4BaNO_2)_2BaHO3H_2O$ requires barium, 43.50 per cent.

Cyano-propionate of Silver.—This salt is insoluble, or sparingly soluble, in water. It was obtained by precipitating an aqueous solution of the baryta salt by means of nitrate of silver, and formed a curdy-white precipitate, which was washed, pressed between bibulous paper, and

finally dried at 100° C. The dried salt was analysed as follows :—

I. 0.395 gramme burnt with oxide of copper, copper turnings, and a final stream of oxygen, gave 0.092 gramme of water and 0.333 gramme of carbonic acid.

II. 1.180 gramme, burnt only for water, gave 0.245 gramme of water.

III. 0.480 gramme gave on ignition 0.246 gramme of silver.

$(C_4H_4NAgO_2)_2\,\frac{1}{2}(H_2O)$.

	Calculated.		Found.		
			I.	II.	III.
C_8 . . .	96	22.80	22.88	...	...
H_9 . . .	9	2.14	...	2.31	...
N_2 . . .	28	6.65	...	...	...
Ag_2 . . .	216	51.31	...	...	51.25
O_{41} . . .	72	17.10	...	...	...
	421	100.00			

The dry silver salt was very hygroscopic, and absorbed 2 per cent. of water very rapidly on exposure to the air.

Apparently a basic silver salt exists, and is obtained when basic baryta salt is precipitated with nitrate of silver. Such a salt, dried in the water-bath, has given the following results on analysis :—

$(C_4H_4NAgO_2)_2AgHOH_2O$.

	Calculated.		Found.	
C_8	96	17.30	17.90	...
H_{11}	11	2.00	2.19	...
N_2	28	...	...	...
Ag_3	324	58.38	...	56.2
O_6	96	...	...	...
	555			

This basic salt requires further investigation.

Cyano-propionate of Lead is insoluble, or sparingly soluble, in water. It is obtained as a white precipitate on mixing an aqueous solution of the baryta salt with an aqueous solution of acetate of lead. The precipitate was washed, pressed between bibulous paper, dried at 100° C., and analysed :—

0.463 gramme, burnt with oxide of copper, gave 0.112 gramme of water and 0.374 gramme of carbonic acid.

$(C_4H_4NPbO_2)_2H_2O$.

	Calculated.		Found.
C_8 . . .	96	22.80	22.00
H_{10} . . .	10	2.38	2.69
N_2 . . .	28		
Pb_2 . . .	207		
O_5 . . .	80		
	421		

Cyano-propionate of Magnesia.—This salt was prepared by precipitating the baryta salt by an equivalent of sulphate of magnesia, separating the sulphate of baryta by filtration, and evaporating the aqueous solution of the magnesia salt in the water-bath. It is very soluble in water, and on drying at 100° C. forms a jelly, which, by very long continued drying at 100° C., yields a brittle mass which may be powdered (giving a white powder). The powder was analysed : 0.863 gramme yielded on ignition 0.132 gramme of magnesia, or 9.18 per cent. of magnesium. The formula $(C_4H_4NMgO_2)_23H_2O$ requires Mg per cent. = 8.90.

The magnesia salt is very sparingly soluble in weak alcohol, an aqueous solution yielding a precipitate when it is mixed with alcohol.

Cyano-propionate of Potash, $C_4H_4NKO_2H_2O$ (dry at 190° C.).—We have prepared this salt by taking a weighed

quantity of the acid (dry at 100° C.), dissolving it in a small quantity of water, and then exactly neutralising the solution with bicarbonate of potash; and we made the observation that the acid requires exactly the theoretical quantity of bicarbonate of potash in order to neutralise it.

The resulting solution of potash salt was evaporated to dryness in the water-bath, and formed a straw-coloured transparent solid. It contained 21.68 per cent. of potassium. The formula $(C_4H_4NKO_2)_25H_2O$ requires 21.47 per cent. of potassium. When the salt is deposited from strong alcohol it dries up at 100° C. to a solid containing rather less water; its composition being $(C_4H_4NKO_2)_24H_2O$. Above the temperature of the water-bath and at temperatures below 140° C., there is a very gradual loss of water; and by prolonged and repeated heating to 190° C. half of the water is driven off and the salt is found to have the formula of

$$C_4H_4NKO_2H_2O,$$

which gave K per cent. 25.21. Experiment gave K per cent. 25.8.

At temperatures higher than 190° C. decomposition began to take place, ammonia and smell of organic cyanides being disengaged. The potash salt undergoes decomposition before it parts with the last atom of water of hydration.

As has already been indicated, the potash salt is exceedingly soluble in water. It is also very soluble in 40 per cent. alcohol, but in strong alcohol (84 per cent. alcohol, for instance) its solubility is very slight.

When the potash salt is heated for some time to temperatures of 200° C. and 220° C., with about one and a half times its weight of caustic potash, it undergoes de-

composition apparently quite completely and ethylamine is given off. On examination of the solid mass after the reaction was over, we found that it contained abundance of oxalate of potash, but we found only minute traces of volatile organic acids. We proved also that the cyano-propionic acid had undergone complete decomposition. We looked carefully for succinic acid, and if present at all, it was not present in appreciable quantity.

The reaction is—

$$C_4H_5NO_2 + 2KHO = C_2O_3K_2O + NC_2H_7,$$

and accordingly the acid is isocyano-propionic acid.

Cyano-propionate of Lime.—We prepared this salt by heating an aqueous solution of the acid with excess of finely divided carbonate of lime, filtering to remove the excess of carbonate of lime, and evaporating the solution of the lime salt in the water-bath. The salt after being dried at 100° C. for some time forms a brittle straw-coloured mass, non-fusible at 100° C. The mass was dried at 100° C. till it became constant in weight. It was then analysed; 0.813 gramme contained 0.1044 gramme of calcium, or Ca per cent. = 12.84. The formula is $C_4H_4CaNO_2$. $2H_2O$ requires Ca per cent. = 12.99.

On raising the temperature this salt shows great stability; and a short heating to 200° C. drives off hardly 4 per cent., which is less than half an atom of water.

The salt is very soluble in water, and on mixing the aqueous solution with an equal volume of 84 per cent. alcohol, gives an abundant powdery precipitate. No doubt this property might be taken advantage of to afford means of purification.

NOTES ON HYDROGEN GAS.

By J. Alfred Wanklyn and W. J. Cooper.

From the *Philosophical Magazine*, November 1890.

The record of some experiments in the laboratory will not be quite without interest to chemists. The wonderful passivity of hydrogen gas is illustrated by the following experiments:—

I. A strong solution of perchloride of iron, made by dissolving the solid chloride in water, was placed in a graduated tube which was inverted in the usual manner so as to form a receptacle for gas. 26 c. c. of hydrogen gas was then introduced into the tube and allowed to remain in contact with the iron solution for forty hours. At the expiration of that time the volume of the gas was found to be unaltered. The gas was then burnt.

II. A solution of platinic chloride containing 5 per cent. of platinic chloride was allowed to act upon hydrogen gas in a Hempel absorption pipette. 95 c. c. of hydrogen was taken for experiment. After twenty-eight hours' exposure the volume of the gas was found unchanged.

III. Ferricyanide of potassium, the solution containing 25 per cent. of the dry salt, was employed in the Hempel absorption pipette. No absorption of hydrogen took place.

A repetition of the experiment in which potash was added to the solution of the ferricyanide, and with exposure to bright sunlight, showed no absorption of hydrogen during a period of eight days.

IV. Nitric acid (sp. gr. 1.42) was tried. An exposure of hydrogen for sixteen hours to the action of the acid produced no change in the volume of the gas, and on examining the gas it was found to be devoid of nitric oxide.

V. A mixture of oil of vitrol and strong nitric acid was altogether without action on the gas.

VI. Aqua regia was also tried and found to be without action on hydrogen. In this case the volume of gas was gradually increased, viz., from 67.5 up to 110 c. c. The increase was due to evolution of chlorine. On washing with water the chlorine was dissolved, and there remained 66.5 c. c. of hydrogen which burnt in a satisfactory manner. This experiment was made in diffused daylight; in bright sunlight reaction between the chlorine and the hydrogen must take place.

VII. Even solution of chromic acid was found to be without action on hydrogen at ordinary temperatures. The duration of the exposure was twenty-four hours, and the readings were :—

Volume of hydrogen	before	64.8 c. c.
„ „	after	65.0 „

The activity of hydrogen is illustrated as follows :—

When solution of permanganate of potash—whether it be strongly alkaline, or neutral, or strongly acid—is brought into an atmosphere of hydrogen, it is attacked by the hydrogen even at ordinary temperatures. The rate of the action depends upon a variety of circumstances which we are carefully studying.

In one experiment the Hempel gas-pipette was charged with a solution containing about 30 per cent. of caustic

potash and about 2 per cent. of permanganate of potash. The readings were :—

Vol. of gas taken . . .	65	c. c.	on	June 24,	1890.
„ after absorption	46	„		June 28,	„
„ „ „	35.8	„		July 2,	„
„ „ „	33.2	„		„ 3,	„
„ „ „	26.8	„		„ 6,	„
„ „ „	21.4	„		„ 10,	„
„ „ „	19.5	„		„ 12,	„

The gas employed in this experiment was a mixture of hydrogen and air, consisting of about three volumes of hydrogen and one volume of air.

It will be noted that at the beginning of the absorption the rate is about 5 c. c. in twenty-four hours; then 2.5 c. c., and lastly 1 c. c. The retardation evidently depends upon the diminishing proportion of hydrogen in the gaseous mixture.

The next experiment was made with a saturated solution of neutral permanganate (containing 6.5 grammes permanganate of potash in 100 c. c. of solution) :—

	c. c.
Volume of gas taken	79.4
After absorption for 26 hours	39.0
„ „ further 14 „	27.4
„ „ „ 12 „	22.8
„ „ „ 13 „	20.8
„ „ „ 24 „	19.8

The gases consisted of :—

Hydrogen	75
Air	25
	100

In this instance the surface of the permanganate solution

was enlarged by the employment of glass beads about 4 millimetres in diameter.

In another experiment the details were :—

	c. c.
Volume of gas taken	29.0
After absorption for 1 hour	25.8
„ „ further 16 hours	10.4
„ „ „ 9 „	6.2
„ „ „ 15 „	5.2
„ „ „ 21 „	5.0

The solution of permanganate was the same as before, and the glass beads were used.

NATURE OF SOLUTIONS AS TO DENSITY OR SPECIFIC GRAVITY.

By J. Alfred Wanklyn, W. Johnstone, and W. J. Cooper.

From the *Philosophical Magazine* for November 1891.

The venerable Dalton made the great discovery, about the year 1840, that contraction occurs when salts dissolve in water. In some instances the contraction is so great that the volume of the solution of the salt is not greater than that of the water itself—the contraction being as large as the volume of the anhydrous salt existing in the solution. Dalton experimented upon the same salt in its hydrated and in its anhydrous condition, and he also extended his investigation to a great number of salts, and his results he sums up as follows:[1]—"I have tried the carbonates, the

[1] Henry's "Life of Dalton" (Cavendish Society), p. 193.

sulphates, the nitrates, the muriates or chlorides, the phosphates, the arseniates, the oxalates, the citrates, the tartrates, the acetates, &c. &c., and have been uniformly successful: only *the water adds to the bulk*, and *the solid matter adds to the weight.*"

Such was the condition in which Dalton left this subject about the year 1840.

Taking up the investigation where Dalton left off, we find that in the majority of cases there is indeed considerable contraction when salts dissolve in water, but that the degree of contraction varies very widely with different salts. In some instances in which mineral matter dissolves in water, the contraction is so great that the volume of the solution is actually less than the volume of the water which forms it. This is strikingly exemplified by lime-water, which occupies less space than the water which it contains. On the other hand, there are cases where the volume of the solution of a mineral salt is almost as great as the sum of the volume of the salt plus the volume of the water in the solution. (The solution of nitrate of silver is a case in point.) There are even instances where expansion takes place. This is exemplified by some ammoniacal salts, where the volume of the solution has been found to exceed the sum of the volumes of water and dry salt.

Finally, there is the very important and, we think, very common case where solution takes place without any change of volume whatever. Such a case is afforded by solutions of cane-sugar,[1] which dissolves in water in almost all proportions, and the solutions of which occupy exactly the

[1] Vide *Chemical News* (1891), vol. lxiv. p. 27, Wanklyn and Cooper.

same volume as the separate water and sugar which enter into them.

A characteristic example of solution is afforded by sugar and water; and we hold that solution is mutual permeation without change of volume, as exemplified by sugar and water.

The changes of volume so frequently observed in the instance of mineral salts are due to chemical action, which is often a concomitant of solution.

In order to trace the connection between the specific gravity of solutions and the composition of solutions, the following method may be followed with advantage.

We regard solutions as being generated by the entrance of successive units of weight into a large unit of volume. The unit of weight is one gramme. The unit of volume is 100 c. c., or one litre. The unit of volume is taken to be constantly filled with the solvent except in so far as it is occupied by the thing dissolved.

i = the increment-coefficient; that is to say, the increment of weight occasioned by the entrance of one gramme of the substance into 100 c. c., or one litre of solution. It is found experimentally by weighing the 100 c. c., or the litre of the solution, and subtracting the weight of 100 c. c. or a litre of the pure solvent. If the solution contains more or less than one gramme of the substance in the 100 c. c. or litre of solution, the number of grammes must be ascertained and used as a divisor.

When one gramme of a substance is inserted into 100 c. c. occupied by a solvent, one of three things must happen :—

(1) There may be absolutely no change in volume—neither contraction nor expansion. When one gramme of

mercury is dropped into 100 c. c. of water, there is neither contraction nor expansion, and the gramme of mercury simply displaces its own volume of water, which overflows out of the 100 c. c. measure. Sp. gr. being the specific gravity of mercury, the quantity of water which overflows will be $\frac{1}{\text{sp. gr.}}$: and the increment of weight in that case would be

$$1 - \frac{1}{\text{sp. gr.}}.$$

Such a value we represent by i_1.

$$i_1 = 1 - \frac{1}{\text{sp. gr.}}.$$

This is the case of sugar, and no doubt of many organic substances which simply dissolve in water without chemical action of any kind.

(2) There may be contraction. This is exemplified by common salt and water. When one gramme of common salt is inserted into 100 c. c. of water, the displaced water is partly condensed and retained in the 100 c. c.

$$i - i_1 = \text{the condensate};$$

that is to say, the weight of the water which, instead of overflowing, is retained in the vessel when one gramme of salt dissolves so as to give 100 c. c. of the solution.

(3) There may be expansion. In such a case, when one gramme enters the 100 c. c. or the litre, a larger quantity than $\frac{1}{\text{sp. gr.}}$ will overflow and

$$i - i_1 \text{ becomes a minus quantity.}$$

This is exemplified by chloride of ammonium, which undergoes decomposition when it is dissolved in water, and the volume of the solution of that salt actually exceeds the sum

of the volumes of the water and the salt in their separate condition.

In a series of papers which have recently appeared in the *Chemical News*, we have treated the solution from this point of view, and show that the condensate $(i - i_1)$, in the case of very many salts, bears an atomic relation to the gramme of salt which occasions it.

Sugar and Water.

The ordinary tables of the specific gravities of solutions of different strengths are constructed so as to mask the regularity of the relation between specific gravity and strength. The common sugar table, for instance, gives the specific gravities corresponding to the strength represented in percentage by weight. That mode of statement hides the regularity; but when the table is transformed so as to set out strength in terms of the number of grammes of sugar in 100 c. c. of solution, then there are indications of regularity. By a very obvious method of calculation this transformation may be effected. The ordinary tables when so treated exhibit some departure from regularity.

We have undertaken a revision of the table, and our result is that these departures from regularity are experimental errors.

Our results are as follows :—

	Number of grms. of Cane-Sugar in Litre of solution.	Specific Gravity.	i
Deg. Fahr.			
65.5	1.341	1000.52	.3878
54.0	1.341	1000.52	.3878
53.7	1.341	1000.52	.3878
53.7	9.878	1003.84	.3887
56.0	104.580	1040.60	.3882
59.0	749.50	1282.00	.3762

In these experiments we have compared the weight of the sugar solutions with the weight of an equal volume of distilled water at the same temperature as the sugar solution, and in each instance have used a half-litre specific-gravity bottle,[1] except in the last experiment.

The last measurement was made with a 100 c. c. bottle, and has not the same claim to be considered highly accurate as the other five measurements; and we attribute the slight difference in that case to experimental error, and to another cause which may be considered hereafter.

The value of i for sugar we find therefore to be .388, and it is constant over a very wide range, viz., from 1 gramme of sugar per litre of solution up to 750 grammes of sugar per litre of solution.

The specific gravity of solid sugar required in order to make $i^1 = .388$ is 1.634. The specific gravity of sugar is given in the text-books as 1.606,[2] which would make $i^1 = .3773$.

Sugar, therefore, presents an example of equality between i and i_1; that is to say, its solutions in water occupy exactly the same volume as the separate water and sugar which form them.

At the beginning of this paper we called attention to Dalton's discovery of the contraction which takes place when salts dissolve in water. Dalton also experimented upon sugar; but failed to notice that in that case there is no contraction; and it has been reserved for ourselves, after the lapse of half a century, to record that there are cases,

[1] *Vide* Wanklyn's "Water Analysis" (Kegan Paul, Trench, Trübner and Co.), eighth edition, p. 78.

[2] *Vide* Watt's "Dictionary of Chemistry," vol. v. p. 470.

such as that of sugar, where there is rigid maintenance of volume.

The following are the values of i (the increment coefficient) for different salts. We give them in order to provide the data for the calculation of the theoretical specific gravity of a complex solution.

The rule for the calculation is this :—

The number of grammes of each salt in one litre of the solution being known, multiply each number by the value i for the salt; add up the products, and the sum is the increment of density for the litre of the mixed solution.

Sodium Compounds.	i.
Chloride, NaCl	.670
Bicarbonate, $NaHOCO_2$	.681
Nitrate, $NaNO_3$	.696
Iodide, NaI	.747
Bromide, NaBr	.757
Sulphate, Na_2OSO_3	.910
Carbonate, Na_2OCO_2	.948
Caustic, NaHO	1.068

Potassium Compounds.	i.
Nitrate, KNO_3	.582
Chlorate, $KClO_3$	.594
Bicarbonate, $KHOCO_2$	.622
Chloride, KCl	.671
Iodide, KI	.702
Sulphate, K_2OSO_3	.784
Caustic, KHO	.841
Carbonate, K_2OCO_2	.849

Lithium Compounds.	i.
Bicarbonate, $LiHOCO_2$	.507
Chloride, LiCl	.810
Caustic, LiHO	1.116

Barium Compounds.	*i.*
Nitrate, $Ba(NO_3)_2$	.782
Chloride, $BaCl_2$	.795
Caustic, $BaOH_2O$	1.120

Calcium Compounds.	*i.*
Nitrate, $Ca(NO_3)_2$	.639
Chloride, $CaCl_2$	.675
Sulphate, $CaOSO_3$	.970
Caustic, $CaOH_2O$	1.290

Magnesium Compounds.	*i.*
Chloride, $MgCl_2$	.833
Sulphate of Magnesia, $MgOSO_3$	.894
Cane-sugar, $C_{12}H_{22}O_{11}$	.388

ON MAGNESIUM.

By J. Alfred Wanklyn and Ernest T. Chapman.

Reprinted from the *Journal of the Chemical Society of London* for the year 1866.

The magnesium met with in commerce appears to be very pure, as is shown by the following determinations of the quantity of hydrogen evolved on dissolving a known weight of the metal in dilute acids. The magnesium ribbon, such as is sold for exhibiting the magnesium light, was employed, having been rubbed first with sandpaper.

I.—0.1275 gramme of magnesium ribbon was dissolved in dilute acetic acid, and the hydrogen evolved was measured—

Observed volume of gas	127 c. c. (moist).
Temperature	11.2° Cent.
Barometer	754.8 millimetres.

Height of the water column in the tube containing the gas corresponding to 0.8 millimetre of mercury.

Tension of aqueous vapour at 11.2° C. = 9.8 millimetres. Correction of the barometer reading, *i.e.* for reduction for temperature = − 1.0 millimetre.

From this we deduce—

Hydrogen = 127 c. c. (dry) at 11.2° C. and 743.2 millimetres pressure.

= 119.31 c. c. dry at 0° C. and 760 millimetres pressure.
= .010665 gramme.

(The weight of 1000 c. c. of hydrogen at normal temperature and pressure being taken at .08939 gramme.)

Taking 12 for the equivalent of magnesium, this will correspond to 0.127980 gramme of real magnesium. Therefore 100 parts of magnesium ribbon contain 100.38 parts of real magnesium.

II.—0.1410 gramme of magnesium ribbon was dissolved in dilute hydrochloric acid, and the hydrogen evolved measured—

Observed volume of gas . . .	141 c. c.
Temperature	11.2° C.
Barometer	754.8 m.m.
Height of water column in millimetres of mercury	= 0.8 m.m.
Tension of aqueous vapour at 11.2° C. .	= 9.8 m.m.
Correction of barometer	= 1.0 m.m.

From which we deduce :—

Hydrogen = 141 c. c. (dry) at 11.2° C. and 743.2 m.m. pressure
= 132.46 c. c. (dry) at 0° C. and 760 m.m. pressure
= 0.011841 gramme,

which corresponds to .142092 gramme of real magnesium.

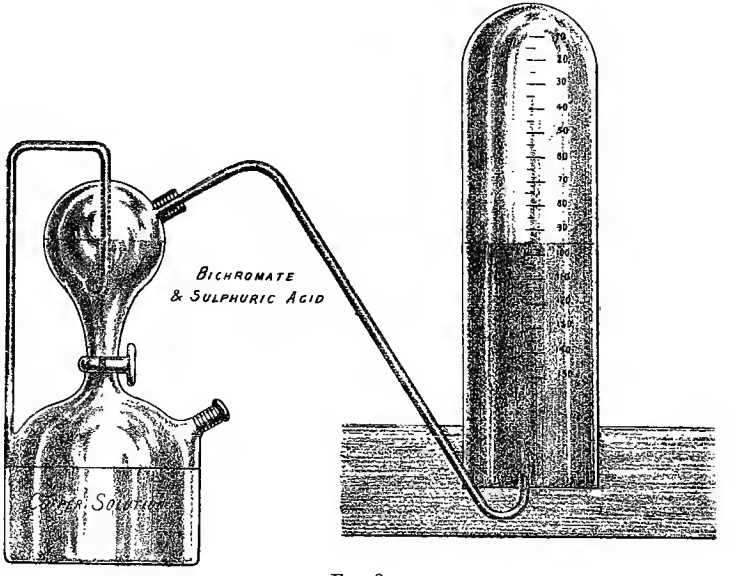

Fig. 8.

Therefore 100 parts of magnesium ribbon contain 100.78 parts of real magnesium.

III.—0.1340 gramme of magnesium ribbon was dissolved in dilute sulphuric acid and the hydrogen evolved measured—

Observed volume of gas	133.2 c. c.
Temperature	11° C.
Barometer.	754.8 m.m.
Height of water column in mercury . .	1.1 m.m.
Tension of aqueous vapour at 11° C. . .	9.8 m.m.
Correction of barometer	1.0 m.m.

From which we deduce—

Hydrogen = 133.2 c. c. (dry) at 11° C. and 742.9 m.m. pressure
= 125.16 c. c. (dry) at 0° C. and 760 m.m. pressure
= 0.011188 gramme,

which corresponds to .134256 gramme of real magnesium. Therefore 100 parts of magnesium ribbon contain 100.19 parts of real magnesium.

The apparatus employed in these determinations was very simple. A small vessel such as is made for determinations of carbonic acid was used for the generation of the hydrogen (see fig. 8).

The upper part of the vessel contained the dilute acid, the lower portion below the glass stop-cock contained water and the weighed magnesium ribbon. The method of using the apparatus, together with the fact that accurate measurements of hydrogen can be made over water saturated with atmospheric air, will be familiar to those who are conversant with the ordinary processes of gas analysis. It will, moreover, be obvious that instead of employing the pneumatic trough, as we did, it is quite practicable to use

the mercurial trough. We are, however, of opinion that in this particular instance there would be no advantage in doing so.

SECTION B.—*Chemical Science.*

ON A PROPOSED METHOD OF PREVENTING THE FERMENTATION IN SEWAGE AND THE FORMATION OF SEWER GASES.

By W. J. COOPER.

Read at the meeting of the British Association at Brighton, Wednesday, August 21st, 1872.

The noxious exhalations arising from the drains of our large cities are daily increasing in volume, and unless some immediate action be taken in order to check the progress of the nuisance, very serious damage to public health will be certain to ensue. Cases of drain-poisoning are not uncommon; and to such an extent has the evil lately spread, that it is difficult to select a thoroughfare in the metropolis which is free from the foul and sickening odour which ascends from every opening and grating communicating with the sewers. Although millions have been expended upon the drainage of London, and it is in contemplation to expend other millions, the evil such expenditure should have allayed has become more serious than ever, and the sewer gases perplexing the engineer by the subtlety of their action, render abortive all his attempts to get rid of them.

In letters which appeared in the *Times* of December last bearing authoritative signatures advice is given for the public use to the following effect. "Dilute the gas with air in every possible direction, and send tall chimneys above the houses to conduct the gases and disperse them." At a time when strenuous efforts are being made to secure purity of atmosphere, when smoke nuisance and other Acts are being rigidly enforced, the idea of building tall chimneys to convey these gases over our dwellings seems unaccountable. The probable effect would be in our heavy atmosphere to spread a sort of miasmatic pall over the metropolis, and as sewer gas in the opinion of some eminent authorities is the vehicle for the conveyance of disease germs, there is a danger of the air above becoming charged with these germs, and these particles being heavier than their envelope (when extended) would descend at intervals, forming a shower anything but refreshing to contemplate; and as we should still be annoyed with the gases below, our sanitary condition would indeed be deplorable.

If a perfect system of drainage (in London) should ever be brought about, as it involves the entire reconstruction of the sewers, it will be many years before the work can be accomplished, and a generation may suffer in the interval from the lack of proper sanitary precaution. It is to chemical agency alone we must look for assistance in this dilemma, and it is perfectly practicable to arrest the fermentation of the sewage during its progress through the conduits and so prevent the evolution of sewer gas. Whilst treating the roads and streets of London and other towns during the last four years with a chloride of calcium mixture, I have found that the waste solution running into the drains has had the effect of pre-

venting the unpleasant ammoniacal odour which it is so desirable to remove.

This led me to further experiments, and I am convinced that at a very moderate cost (about one shilling annually per head of population) the sewers of London and other large towns could be rendered perfectly free from sewer gas. I propose to apply a chloride of calcium preparation in a powdered form or in solution to the openings immediately in connection with the sewers at times when the sewers are nearly empty, and especially in times of drought. The effect of chloride of calcium upon carbonate of ammonia causes the decomposition of the latter and the formation of the neutral salts of chloride of ammonium and carbonate of lime. But by treating the sewers at proper times with a chloride of calcium mixture, the generation of ammonia and its accompanying products of decomposition would be prevented.

Ammonia is generated in the sewers by the decomposition of urea in the presence of water. The progress of this decomposition consists in the fermentation of the urea, urea plus water being equal to carbonate of ammonia. From the results of further experiments (corroborating my previous experiences) there is no doubt that a moderate quantity of the chloride of calcium mixture, which is cheap and inodorous, will effect the required object of arresting the fermentation of the urea and the evolution of noxious gases.

At the Pharmaceutical Conference last week Mr. Stanford read a paper on "the power of different disinfectants," and showed, as the result of his investigations, that chloride of calcium was the most practical and powerful of all disinfectants, being cheap, abundant, effective, free from any odour

or danger in its use, which latter quality is essential to the popular utility of a deodorising agent.

I have good reason to expect that this practical process will soon be tried on a very extensive scale in one of our largest towns, and I look with confidence to the result which I have no doubt will occur, viz., the reduction of the death-rate, which at present is excessive owing in a great measure to the deleterious effects of sewer gas.

SOCIAL SCIENCE CONGRESS—HEALTH DEPARTMENT.

On the Defilement of Air.

Paper read at Norwich, October 4, 1873, by W. J. Cooper.

Air, to be fit for respiration, must be of an extraordinary degree of purity. The combined efforts of sanitarians should be directed to secure this object. It is to be regretted that some well-meaning workers in sanitary science recommend a course of action which (by adding noxious vapours to impure air for disinfecting purposes) not only increases the previous defilement, but prevents clarification, which is the main object to be attained.

Air cannot be charged with any volatile vapour without detriment, whether it be sewer gas from the drains, carbonate of ammonia from horse-droppings, aroma from the dust-cart, or the equally vile odour which arises from weak solutions of carbolic acid, now used in some towns with the idea that it will destroy the germs of disease. Eminent authorities have

proved the fallacy of this notion. Carbolic acid in a concentrated form will arrest decomposition for a while, but Pettenkofer's experiments have clearly shown that when the acid is further diluted, germ development is actually encouraged. Dr. Dougall's recent experiments have exposed the futility of the use of the vapour of carbolic acid on infective matter; and it is also known that during the Franco-German war, although hospitals were saturated with carbolic acid, still hospital gangrene prevailed. With these facts before us, it is intolerable that the air of our public places, our dwellings, and our towns should be daily defiled by volatile vapours arising from this objectionable substance with the vain expectation of preserving the public from infection, the effect being to encourage a rather expensive method of creating a nuisance. Where carbolic acid is used, it cannot be always ascertained whether the stench operated upon is removed or not, but we know that when applied to urinals the sickly ammoniacal odour is not affected, the twofold atmospheric defilement of the carbolic acid and ammoniacal odours being distinctly and separately distinguishable. There is much evidence to show that you cannot impregnate the air with a vapour sufficiently powerful to destroy germs or infectious matter without damage to the tissue of the lungs. Liebig has stated that lung disease was produced by the use of chlorine as a disinfectant in hospitals.

In the last published number of the *Proceedings of the Chemical Society* it is related that Mr. Ernest Theophron Chapman, an eminent chemist, who recently lost his life by an explosion in a chemical manufactory in Germany, had suffered in health for many years from the effects of

the inhalation of chlorine, which brought on hæmorrhage from the lungs, a complaint which would frequently recur when he was under the influence of any excitement.

It is also known that the strong Highland workmen employed at the St. Rollox Works in Glasgow are rapidly destroyed by the chlorine vapour given off from the bleaching powder manufactured there. Bromine, iodine, and ozone are equally mischievous in their action. Before you could use enough iodine to have any effect upon germs, it will produce the well-known iodine catarrh. Bromine would overpower the senses with its suffocating stench long before it could disinfect; and if the atmosphere was to be overcharged with ozone, it would be productive of equally deleterious consequences.

Recent investigations have fully exposed the futility of several methods practised with the intention of destroying the germs of disease by attempting the impossible task of disinfecting air. These delusive theories have been based upon the fallacious supposition that a chemical reagent retains its destructive power when very dilute. Experience has shown that the very reverse happens in many instances. Strong sulphuric acid will set fire to wood shavings, and so destroy them. Dilute sulphuric acid will transform shavings into grape-sugar, which is susceptible of fermentation. This is an illustration which holds good throughout organic chemistry. Professor Rolleston informs us, that unless sulphurous acid be put into the air of a room so that no one could exist in it for a minute, all fumigation is abortive. Professor Wanklyn in a recent paper on disinfectants observes that the wisdom of the physician who places his little saucer with bleaching powder and muriatic acid in

the chamber of his patient is comparable with that of the Cattle Plague Commissioners, who tied carbolised cloths to the horns of the cattle to disinfect the air of the agricultural districts. If the air of a room be foul, the obvious remedy is to open the window to let in the external air, as the best possible purifier. If the room contain germs, they will probably find surfaces to rest upon, and it is by cleansing all surfaces that the room is to be purified, and not by futile attempts to disinfect an ever-changing atmospheric current.

All germs of disease must be looked upon as a dangerous enemy, they must be treated as an invading army and deprived of every possible feeding and resting place. As they are fostered in filth and putridity, all filth and decaying matter should be carefully removed, and decomposition should be arrested in sewers, on road surfaces, and in holes and corners where putrefying matter of any kind is deposited.

For the purpose of arresting decomposition, chemical substances should be used which do not by their nature defile the air, and are not dangerous, destructive, or offensive; for it is of the utmost importance to make disinfection popular, and it is contrary to human nature to delight in substances which are so irritating and obnoxious to the senses, and which have a tendency to cause a positive evil in the attempt to prevent a possible one.

ON THE COMPARATIVE EFFECT OF LIME AND OTHER CHEMICALS UPON SEWAGE.

By J. Carter Bell.

The following are the results of many months' experiments, carried out under similar conditions as to quantities, time, and temperature. In the first instance, experiments were carried out in the laboratory upon 700 c. c. of settled sewage, this quantity being convenient as it represented 10 gallons. From the table annexed it will be seen that other chemicals were tried in comparison with lime, in order to find out the best precipitant, and one which gave the least amount of sludge.

Antinonnin, mercuric chloride, and acetate of lead were used merely from scientific curiosity, and these expensive chemicals did not produce such good results as the cheaper lime.

In the case of powerful antiseptics, such as mercuric chloride, hydrogen peroxide, &c., no physical change was apparent: the sewage was sterile but very unsightly. This perhaps would not matter if all the works in the watershed produced sterile effluents; but it is undoubtedly pleasant to look upon a bright and sparkling effluent.

Turning to the cheaper chemicals in this table, it will be observed that there is very little difference in the percentages of purification.

Lime has a bad name, but that arises from not knowing how to use it. People think that if an effluent shows an alkalinity of one or two grains to the gallon, enough lime has been used, which is a mistake. It is natural that

when you have excess of lime present, all that can be precipitated by lime is thrown down. The lime does not follow the usual rule. In the table annexed this is plainly seen.

The five experiments in Table II. were made upon the same sample of settled sewage as the precipitant. The lime was used in the proportion of 10, 15, 20, 25, and 30 cwt. to the million gallons of sewage.

With 10 cwt. per million gallons giving 3 grains of lime in excess, very little purification took place, the effluent looking very much like the original sewage; and even 15 cwt. did not give a brilliant effluent. It was not until 20 cwt. was reached that any satisfactory purification took place, and in this case an increased quantity of lime failed to effect any further improvement in albuminoid ammonia and absorbed oxygen. A small quantity of lime added combines with the dissolved carbonic acid, and is thus lost, and can have no effect upon the dissolved organic matter.

The lime may vary in quality, as the following sample will show :—

	No. 1.	No. 2.	No. 3.	No. 4.
Lime	92.55	98.14	85.21	88.64
Carbonate of lime .	9.12	1.21	12.62	10.22
Silica, alumina, and iron	0.24	0.31	0.18	0.23
Water	0.01	0.33	1.99	0.91

No. 3 sample badly slaked would give very poor results.

According to some authorities, the strength of the solution varies according as more or less water has been used to slake the lime. I do not agree altogether with the above, but the amount of water used for slaking has a

considerable influence upon the resulting milk of lime. It was the custom formerly at Salford to dry-slake the lime, and then to sift it and mix with water; a dangerous method for the workmen, who had to work with cloths tied over their mouths in an atmosphere of lime-dust. I advised the Committee to adopt wet slaking of the lime, with the result of producing a much better milk of lime. I have found that 1 part of lime to 4 parts of water disintegrates the lime into an impalpable powder. Four experiments were performed with 1 part of lime to 1, 2, 3, and 4 parts of water. The first was in the granular condition; the second partially so; and three and four were in an impalpable powder.

	Grains per gallon. 15 minutes.	Grains per gallon. 12 hours.
No. 1 contained .	106.4	93
„ 2 „ .	105.0	93
„ 3 „ .	103.6	93
„ 4 „ .	102.2	93

The four were made up in the same bulk with water, allowed to settle for fifteen minutes and twelve hours.

Given a slight excess of lime, 1 c. c. of the lime-water will contain from .00125 to .0013 grammes of lime, or about 90 grains to the gallon. But it does not follow, if one weighs out the quantity of lime which is equivalent to the 90 grains, that one will have a water equal to that strength.

The objectors to lime as a sewage purifier say that it dissolves organic matter, and that the resulting effluent contains more organic matter than the original sewage. Now if you

TABLE I.

The Comparative Action of Various Chemicals upon the same Sample of Clear or Settled Sewage.

	Free Ammonia.	Albuminoid Ammonia.	Appearance.	Per Cent. of Purification.	Oxygen required for 4 Hours.	Per Cent. of Purification.
	Grs. per Gall.	Grs. per Gall.			Grs. per Gall.	
Settled sewage	2.2	0.76	Black	..	5.6	..
„ filtered through paper	2.2	0.48	Opalescent	37	4.2	25
Chloride of iron filtered through paper	2.0	0.16	Clear	79	2.4	57
Antinonnin	2.0	0.16	„	79	3.2	43
Hydrogen peroxide	2.0	0.44	Opalescent	42	1.5	73
Mercuric chloride	2.0	0.76	Very cloudy	Nil	5.6	Nil
Chlorine	1.6	0.32	Cloudy	57	3.1	44
Sodium peroxide	2.0	0.68	„	10	5.0	10
HCl and MnO_2	0.12	0.08	Clear	89	2.1	62
$FeSO_4$ and lime	2.3	0.18	„	76	1.8	67
HgCl and lime	1.2	0.04	„	94	0.7	87
$FeSO_4$	2.0	0.76	Cloudy	Nil	5.3	5
Perchloride of iron and lime	2.0	0.24	Clear	68	2.0	64
Carbolic acid	2.2	0.76	Black	Nil	20.5	Nil

TABLE II.

[All results are in grains per gallon.]

	Sewage.	10 Cwt.	15 Cwt.	20 Cwt.	25 Cwt.	30 Cwt.
Appearance	Black	Very like sewage.	Cloudy	Clear	Clear	Clear
Free ammonia	1.6	1.2	1.0	1.0	1.0	1.0
Albuminoid ammonia	0.64	0.56	0.36	0.28	0.28	0.28
Per cent. of purification	...	12.5	43.7	56.2	56.2	56.2
Oxygen for 4 hours	5.1	4.2	3.4	2.4	2.3	2.3
Free lime in effluent	...	3.0	4.5	5.5	7.0	8.0
Total dry sludge	...	21.7	30.5	39.0	41.0	41.0
Tons to million gallons, containing 10 per cent. of total solids	...	13 tons 16 cwt.	19 tons 9 cwt.	24 tons 17 cwt.	26 tons 2 cwt.	26 tons 2 cwt.
Mineral matter	...	18.7	24.0	30.2	31.2	32.0
Organic matter	...	3.0	6.5	8.8	10.1	9.0
Lime in sludge	...	11.2	15.0	18.0	18.0	19.0

compare the analyses of the effluents which I have placed before you—the 20 cwt., 25 cwt., and 30 cwt. of lime to the million gallons—the latter ought to contain considerably more organic matter than the former; but they are all much the same in regard to albuminoid ammonia and the oxygen test, though the lime rises from 5 to 7 and 8 grains to the gallon. The amount of sludge precipitated also rises from about 14 tons to 26 tons to the million gallons, the difference being between 10 cwt. of lime and 30 cwt. In each case 150 or more million gallons were used.

In the first experiment 20 cwt. of lime was used, and over 4000 tons of sludge was produced; in the second experiment, where no lime was used, only about 1000 tons of sludge was precipitated in the tank. The difference of 3000 tons must be due to the purifying action of the lime, therefore it seems absurd to say that lime has no purifying action.

Laboratory experiments showed that sulphate of alumina or persulphate of iron was the best to use as regards the amount of sludge formed, for in these cases only a little over 4 tons was produced, whereas in the cases of lime and baryta the quantities were 25 and 30 tons respectively. This means a cost for removal of sludge of, say, 1s. a ton, though it does not cost quite so much. The alumina treatment, according to these experiments, would cost about 30s. the million gallons, whereas the lime would be over 40s. As a result of these laboratory experiments, I advised the Committee to use sulphate of alumina. When this experiment was carried out with 167 million gallons, which were flowing for fourteen days, and to each million gallons were

TABLE III.

Experiments on Settled Sewage to determine the best Chemical Sewage Precipitant and that giving the least Sludge.

[All results are in grains per gallon.]

Quantity for One Million Gallons.	Free NH_3.	Albuminoid Ammonia.	Percentage of Purification.	Oxygen, 4 Hours.	Lime.	Precipitated Sludge.	Mineral.	Organic.	Tons of Sludge to Million Gallons containing 90 per Cent. of Water. Tons.	Cwt.
10 cwt. lime, 15 cwt. copperas . . .	1.2	0.14	50	0.95	Nil	28.3	23.1	5.2	17	12
25 cwt. lime . . .	1.2	0.11	60	0.81	3	41.1	34.7	6.4	25	12
15 cwt. alumina . .	1.5	0.11	60	0.89	Nil	7.5	3.4	4.1	4	12
5 cwt. lime, 15 cwt. alumina	1.5	0.11	60	0.98	Nil	7.3	4.1	3.2	4	10
25 cwt. Wardle persulphate of iron .	1.5	0.11	60	0.70	Nil	8.1	4.0	4.1	5	0
25 cwt. barium . .	1.5	0.11	60	0.95	BaO6	47.3	42.8	4.5	30	0
25 cwt. lead A . .	1.6	0.11	60	1.0	Nil	26.4	20.0	6.4	16	10
25 cwt. mercuric chloride . . .	1.6	0.28	Nil	2.5	Nil	Nil	Nil	Nil	Nil	
25 cwt. chloride of lime	1.7	0.29	Nil	2.6	Nil	Nil	Nil	Nil	Nil	
25 cwt. carbolic acid	2.0	0.31	Nil	2.8	Nil	Nil	Nil	Nil	Nil	
25 cwt. sulphurous acid	1.6	0.28	Nil	6.5	Nil	Nil	Nil	Nil	Nil	

added 18 cwt. of sulphate of alumina, the quantity of sludge formed was 4923 tons. Samples of sewage and effluent were taken every hour for the fourteen days, and at the end of each day the samples were mixed so as to obtain the average for the day. The daily sample was analysed, and at the end of the fourteen days the average was taken of the albuminoid ammonia and the oxygen required for four hours.

	Grains per Gallon.
Average albuminoid ammonia in sewage . .	0.33
„ „ „ effluent . .	0.22
Percentage of purification, 33.	
Average oxygen required for four hours' sewage.	3.1
„ „ „ „ effluent	2.1
Percentage of purification, 32.	

	Grains per Gallon.	
	Sewage.	Effluent.
The highest amount of albuminoid ammonia in the sewage and the effluent for the 14 days was	0.50	0.28
The lowest was . . .	0.22	0.17
Highest oxygen required for 4 hours	4.1	3.0
Lowest oxygen required for 4 hours	1.7	1.2

At the commencement of this experiment six clean tanks were prepared, holding about two and a half million gallons. These tanks were nearly 700 feet long, about 8 feet wide, and varied in depth from 5 to 8 feet. The treated sewage ran into No. 1, then into No. 2, and so on to No. 6, whence it flowed into the Ship Canal.

It will be interesting to note the quantity of sludge in

each tank at the end of the fourteen days, and the amount of solid matter in the sludge, mineral and organic.

Tank.	Tons of Sludge.	Total Solid Matter at 212° F.	Mineral.	Tons of Dry Solid Matter.
No. 1 . .	827	8.5	4.1	70.3
„ 2 . .	1,506	4.3	1.8	64.7
„ 3 . .	1,496	3.4	1.3	50.8
„ 4 . .	816	3.1	1.2	25.3
„ 5 . .	178	4.5	1.2	8.0
„ 6 . .	100	3.2	1.2	3.2

The average amount of total solids in this sludge was 4.5 per cent. This alumina sludge was allowed to stand at rest for twelve days, so that some of the water might separate.

1st day . .	8 volumes of water	7th day . .	20 volumes of water
2nd „ . .	12 „ „	8th „ . .	21 „ „
3rd „ . .	14 „ „	9th „ . .	22 „ „
4th „ . .	16 „ „	10th „ . .	23 „ „
5th „ . .	18 „ „	11th „ . .	23 „ „
6th „ . .	19 „ „	12th „ . .	23 „ „

This keeping of the sludge would raise the total solids to a little over 5.5 per cent.

Next 179 millions of gallons of sewage were treated with sulphate of alumina and lime in the proportions of 9 cwt. 22 lb. alumina sulphate and 8 cwt. of lime to the million gallons.

	Grains per Gallon.
Average albuminoid ammonia in sewage . .	0.326
„ „ „ effluent . .	0.245
Percentage of purification, 25.	
Average oxygen required for four hours' sewage	2.9
„ „ „ „ effluent	1.9
Percentage of purification, 34.	

Sludge formed in the Six Tanks.

Tank.	Tons of Sludge.	Total Solid Matter at 212°F.	Mineral Matter.	Organic.	Tons of Dry Sludge.
No. 1	1,254	18.1	10.2	7.9	227.0
„ 2	1,534	14.5	7.4	7.1	222.5
„ 3	1,449	8.7	4.1	3.6	126.0
„ 4	116	8.5	4.6	3.9	9.86
„ 5	67	10.7	4.3	6.4	7.17
„ 6	34	21.0	11.4	9.6	7.14

The sludge here was much higher in total solids than in any other experiment, due to the heavy rainfall (2.02 in.) during the fourteen days.

As this experiment was not wholly satisfactory, owing to the large quantity of solid matter washed into the tanks, it was decided to try another fourteen days' test, with sulphate of alumina and lime in about the same proportions.

	Grains per Gallon.
Average albuminoid ammonia in sewage . .	0.357
„ „ „ effluent . .	0.245
Percentage of purification, 31.	
Average oxygen required for four hours' sewage	2.6
„ „ „ „ effluent	1.7
Percentage of purification, 34.	

These two experiments are remarkably close as regards the purity of the effluents. Taking the oxygen percentage purification, the numbers are identical, and the albuminoid ammonia the same in both experiments.

But the amount of sludge in the tanks was widely different. Instead of 4454 tons, there was now 3028 tons. The rain for this fortnight was only 0.506 in., against 2.019 in.

Quantity of Sludge in Tanks from Alumina and Lime Effluent.

Tank.	Tons of Sludge.	Total Solid Matter at 212° F.	Mineral.
No. 1	806	11.3	6.4
„ 2	1,229	9.1	5.4
„ 3	504	8.5	4.5
„ 4	197	7.0	3.6
„ 5	128	8.0	4.3
„ 6	164	8.0	3.9

The quantity of sewage purified during the fourteen days was 168 million gallons, which deposited 3028 tons, or 18 tons to the million gallons.

A fourteen days' experiment was tried with sulphate of iron and lime. The quantity of sewage treated was 166 million gallons. For each million gallons was used 14 cwt. of sulphate of iron and 7 cwt. 1 qr. of lime.

Tank.	Tons of Sludge.	Total Solid Matter at 212° F.	Mineral.
No. 1	1,095	9.5	4.7
„ 2	1,538	4.4	2.4
„ 3	636	4.2	2.0
„ 4	824	4.2	2.1
„ 5	518	6.1	2.8
„ 6	316	6.7	3.0

The quantity of sludge formed in the tanks was 4927 tons.

After sixteen days' settling, the average sludge gave 41 volumes of water. The analysis of this water was :—

	Grains per Gallon.
Free ammonia . . .	6.7
Albuminoid ammonia . .	4.7
Oxygen required for four hours	10.2

The highest albuminoid ammonia in grains to gallons of

the sewage was 0.39 and the lowest was 0.25. The average of the fourteen days was 0.30.

Highest albuminoid ammonia in effluent was 0.30. The lowest was 0.22. The average of the fourteen days was 0.27.

This is rather a poor result, as the purification is only a little over 9 per cent.

The oxygen purification gives a better result.

The average oxygen number in grains per gallon for the settled sewage was 3.4 and in the effluent 2.3, or a percentage purification of 32.

A fourteen days' experiment was tried with chloride of lime or bleaching-powder, using 1 cwt. per million gallons. This quantity was too small to precipitate any of the organic matter in solution, and the sludge which was formed in the tanks was simply due to the suspended matter. The quantity of sewage treated was 150 million gallons during the fortnight, and 1120 tons of sludge was deposited in the tanks.

Tanks.	Total Solid Matter at 212° F.	Mineral Matter.	Organic Matter.
No. 1	13.4	6.8	6.6
„ 2	13.7	7.4	6.3
„ 3	12.3	6.6	5.7
„ 4	12.8	7.4	5.4
„ 5	11.8	6.6	5.2
„ 6	11.1	6.2	3.9

The sludge on standing gave 26 volumes of water after seven days.

First day	13	volumes.
Second day	18	„
Third day	22	„
Fourth day	23	„
Fifth day	24	„
Sixth day	25	„
Seventh day	26	„

On the eighth day it decomposed and mixed with the supernatant liquid.

The above experiment was interesting as it proved conclusively that lime has the power of precipitating organic matter from solution, for in no fortnightly experiment with lime was so small a quantity of sludge formed as above.

Thus :—

Million Gallons of Sewage.							
168	with	144	tons of	lime	gave	4,742	tons of sludge.
162	„	150	„	„		4,211	„ „
150	„	145	„	„		4,100	„ „
160	„	153	„	„		4,427	„ „
150	„	154	„	„		4,836	„ „
179	„	121	„	„		3,882	„ „
173	„	109	„	„		3,404	„ „
145	„	135	„	„		3,684	„ „

In all my small and large experiments I have found that lime is able to precipitate 30 or 40 per cent. of the soluble organic impurity, which is as much as the other precipitants were able to do.

To produce a good clear effluent, there should be at least from 8 to 10 grains of lime in the gallon of effluent in excess. A small quantity of lime effects very little purification, as the following experiments will show :—

Two million gallons of sewage were treated daily for some days with from 30 to 40 cwt. of lime to the million gallons, and eight millions were treated with 10 cwt. of lime to the million gallons. The two effluents were allowed to flow away side by side down an incline plane, and the contrast was most remarkable; on one side there was a dark turbid stream, while on the other there was a bright clear effluent.

The following analyses show the effect of a free use of lime :—

Lime, 10 Cwt. to Million Gallons.		Lime, 30 Cwt. to Million Gallons.	
Albuminoid Ammonia.	Oxygen required for 4 Hours.	Albuminoid Ammonia	Oxygen required for 4 hours.
Grains to Gallon.	Grains to Gallon.	Grains to Gallon.	Grains to Gallon.
0.22	3.2	0.11	1.4
0.25	3.4	0.14	1.5
0.28	3.8	0.12	1.3
0.21	2.8	0.09	1.2
0.23	3.0	0.11	1.4
0.29	3.6	0.12	1.4

The lime varied from 1 to 2 grains to the gallon in the 10-cwt. experiments, and from 8 to 12 grains in the 30-cwt. experiment.

Two million gallons of sewage were treated with about 30 cwt. of lime to the million gallons, and the effluent was allowed to flow into six tanks. It was allowed to rest there for four hours; at the end of that time sewage and effluents were analysed, with the following results:—

	Free Ammonia.	Albuminoid Ammonia.	Per Cent. of Purification.	Oxygen for 4 Hours.	Per Cent. of Purification.	Lime.
	Grains per Gallon.					
Sewage.....	1.7	0.56	...	3.9	...	Nil.
Effluent, No. 1 tank	1.1	0.25	55	1.8	53	12.3
Effluent, No. 2 tank	1.2	0.25	55	1.8	53	10.3
Effluent, No. 3 tank	1.2	0.22	60	1.9	51	10.0
Effluent, No. 4 tank	1.2	0.28	50	1.9	51	10.0
Effluent, No. 5 tank	1.4	0.25	55	1.8	53	10.0
Effluent, No. 6 tank	1.4	1.7	69	1.8	53	12.0

The following twelve samples of effluents were taken from twelve separate tanks after standing four hours. The sewage had been treated with about 25 cwt. of lime, and after the mixture had travelled along a channel of 700 ft. in length before running into the tanks. It seems that to obtain the best results a certain quantity of lime is necessary; all above that is so much waste. Thus it will be seen from the following table that the effluent which contains the most lime is not better than the one which contains half the quantity. The quantity of sewage treated in this experiment was five million gallons, and one would have expected that the quantity of lime would have been the same in each tank. The cause of this difference is the bad mixing of the lime with the sewage. This is one of the causes of the poor results sometimes obtained from lime precipitation:—

	Free Ammonia.	Albuminoid Ammonia.	Oxygen for Four Hours.	Lime.	Appearance of Effluent.
	Grains to Gall.	Grains to Gall.	Grains to Gall.	Grains to Gall.	
Sewage . .	1.9	0.45	3.9	...	...
Effluent No. 1 tank . .	1.8	0.30	2.2	4.6	Clear; slight sediment.
No. 2 north tank	1.5	0.39	2.5	4.9	,, ,,
,, 3 ,,	1.7	0.36	2.4	7.8	,, ,,
,, 4 ,,	1.5	0.33	2.2	7.8	Clear; no sediment.
,, 5 ,,	1.5	0.33	2.1	9.8	,, ,,
,, 6 ,,	1.7	0.30	2.2	11.7	Very clear.
No. 1 south tank	1.7	0.25	1.9	5.8	Clear.
,, 2 ,,	1.8	0.19	1.6	6.3	,,
,, 3 ,,	1.8	0.30	2.0	6.3	Clear; slight sediment.
,, 4 ,,	2.2	0.30	2.1	10.2	Clear.
,, 5 ,,	2.2	0.36	2.5	4.9	Rather cloudy.
,, 6 ,,	2.1	0.39	2.8	1.4	Very cloudy with sediment.

Many managers think if the milk of lime is run into the inlet channel with the sewage, that it is quite sufficient to make homogeneous mixture. This is not the case, for the lime will often be carried along in a certain current, and in all parts of the channel the lime will be in variable proportion. That this is so is shown by the following three experiments. Samples of the effluent were taken at six equidistant places along the channel, and the lime estimated in grains per gallon :—

No. 1. Not Mixed.			No. 2. Well Mixed.			No. 3. Not Mixed.		
17.0	6.5	14.5	8.2	8.0	8.0	10.5	14.0	9.5
19.0	6.0	15.5	8.0	8.2	8.0	10.0	12.0	9.0
21.0	6.0	16.5	8.0	8.0	8.0	10.0	7.5	10.0
23.0	6.0	14.0	8.0	8.5	8.0	11.0	7.5	11.0
10.0	6.5	14.5	7.5	8.0	8.0	11.0	8.0	11.0
10.5	10.0	15.0	7.0	7.5	8.5	8.0	7.5	10.5

The three sets of figures in each experiment represent samples taken from the centre of the channel and the two sides. It is most important that the chemicals and sewage be thoroughly mixed before dilution, for if the latter takes place the lime fails to precipitate organic matter. The lime falling to the bottom of the channel is soon converted into carbonate of lime, and is thus lost. In the channel already spoken of, the precipitated lime was estimated in the sludge formed at six different places. No. 1 was point of inlet, and No. 6 was the point of outlet, the other numbers being equidistant between.

No. 1 dry sludge contained 12.6 per cent. of lime
" 2 " " 19.6 " "
" 3 " " 16.8 " "
" 4 " " 24.7 " "
" 5 " " 24.7 " "
" 6 " " 32.0 " "

I have always advocated the use of lime-water to prevent this great waste of lime; much better results can be obtained than by the use of solid lime.

The experiments in the following table were made on different days with lime and lime-water, using the same sewage in both cases, and the same quantity of lime. The quantity of lime used has been 25 cwt. to the million gallons.

In every experiment the lime-water has given the best results, amounting sometimes to as much as 50 per cent. improvement. In all these precipitation processes there seems to be a number which the precipitant cannot attack. The albuminoid ammonia falls to about 0.14 in the gallon, and there remains, and no addition of ordinary cheap chemical seems to disturb that number; as fortnightly experiments have been tried with sulphate of alumina, iron, &c., it became necessary for comparison-sake to try similar experiments with varying quantities of lime; it will be sufficient if the minimum and maximum lime experiments are given in detail.

Lime Water.			Solid Lime.		
Albuminoid Ammonia.	Oxygen for 4 Hours	Lime.	Albuminoid Ammonia.	Oxygen for 4 Hours.	Lime.
Grains to Gallon.	Grains.	Grains to Gallon.	Grains to Gallon.	Grains.	Grains to Gallon.
0.17	1.5	3.5	0.25	2.6	4.0
0.14	1.4	4.4	0.30	2.3	6.2
0.14	1.6	3.9	0.28	2.4	3.2
0.22	1.9	3.0	0.28	2.8	4.2
0.22	1.4	8.8	0.25	2.6	9.2
0.14	1.2	9.3	0.19	2.3	7.8
0.14	1.5	6.8	0.21	2.4	5.5
0.20	1.8	4.0	0.25	2.6	3.5

The number of gallons of sewage treated in this No. 1 lime experiment was 173 millions. Rainfall for the fourteen days was 1.601 inches. Quantity of lime used to one million gallons was 12 cwt. 2 qrs.

The maximum albuminoid ammonia in the sewage in grains to gallon was 0.22.

The average for the fortnight was, for sewage 0.34, and for effluent 0.31.

This, practically speaking, gave no purification, only about 8 per cent.

The average oxygen required for four hours was—sewage, 2.6 grains to gallon, and effluent 2.4 grains to gallon.

	Tons.	Total Solids.	Mineral.
No. 1 tank contained .	786	11.6	7.2
,, 2 ,, ,, .	1204	9.1	6.0
,, 3 ,, ,, .	373	13.6	8.6
,, 4 ,, ,, .	412	11.6	7.3
,, 5 ,, ,, .	330	13.6	6.7
,, 6 ,, ,, .	299	12.8	6.1

Only 7 per cent. of purification. The quantity of sludge formed in the tanks was 3404 tons.

The second lime experiment was about 20 cwt. to the million gallons; sewage treated, 162 million gallons; rainfall for the fourteen days, 0.740 inch. Average albuminoid ammonia in settled sewage, 0.402 grains per gallon; effluent, 0.278; which gives a purification of 30 per cent.

The average oxygen required for four hours was, sewage 3.2 grains to gallon, and effluent 2.1 grains to gallon, or a purification of 34 per cent. The quantity of sludge formed in the tanks was 4211 tons.

	Tons.	Total Solids.	Mineral.
No. 1 tank contained .	518	10.8	7.2
,, 2 ,, ,, .	1523	9.3	5.9
,, 3 ,, ,, .	1103	7.2	3.9
,, 4 ,, ,, .	671	5.9	3.8
,, 5 ,, ,, .	224	8.2	3.9
,, 6 ,, ,, .	172	8.9	5.3

The average sludge gave, after standing for one week, 23 volumes of water.

On comparing the lime effluents and percentages of purification with the effluents from the sulphate of alumina and sulphates of iron, very little difference is found when a sufficient quantity of lime is used. It is remarkable that the first five tests should work out so closely in regard to the oxygen purification test, for, practically speaking, it is nearly the same in each, 34 per cent.

For comparison-sake I have included in the following table the electrical process, though the whole of the sewage was not purified by this process. This experiment was carried on for seventy-two days, and during this time $7\frac{1}{4}$ million gallons were treated. The weight of sludge was, in round numbers, 120 tons, or $16\frac{1}{2}$ tons to the million gallons. This quantity includes the solid matter which was in the sewage in suspension, and which amounted to many tons. This being deducted, leaves so many tons precipitated from the iron plates which were used as electrodes. This quantity was easily calculated. The number of plates was 2176; each plate measured 2 ft. by 1 ft. 6 in. by $\frac{1}{2}$ in. The weight of these plates before the commencement of the experiment was 54 tons; at the close of the experiment they

were taken out, dried, and weighed. The weight was 53 tons 7 cwt. 0.14 lbs. The plates were covered with oxide of iron; this was all cleaned off, and after this the plates weighed 52 tons 4 cwt. 2 qrs. 14 lbs., showing a loss of 1 ton 15 cwt. 1 qr. 24 lbs.; this gives a little over three grains to the gallon of sewage. The average albuminoid ammonia from 52 samples was 0.168 grain to the gallon, and the percentage of purification had been 39. This is higher than any in the list; but, on the other hand, one must notice the cost, which is £3 the million gallons, this being nearly the highest in price. The extra 5 per cent. of purification would hardly warrant the extra expenditure. This is a very neat and elegant process, and when joined to filtration the effluents are all that one would desire.

In one respect the sludge is not utterly useless, for consisting so largely of oxide of iron, it has been made into paint by calcination. This was tested by a manufacturer of paints, who reported that it made a good oxide of iron paint, but not equal to the best brands upon the market.

The composition of the calcined sludge is—silica, 30.95; ferric oxide, 47.80; alumina, 8.52; carbonate of lime, 9.12; phosphoric acid, magnesia, alkalies, 3.61.

Experiments were made upon sewage to which 10 cwt. of lime were added to the million gallons; it was then treated by the electric current. These experiments were not successful, the percentage of purification being only 27.

TABLE IV.

Sewage in Millions of Gallons.	Rain-fall.	Chemicals to One Million Gallons.	Total Quantity of Sludge in Tanks.	Total Quantity calculated to contain 10 per Cent. of Total Solids.	Quantity of Sludge to One Million Gallons, 10 per Cent. of Total Solids.	Average Total Solids of Sludge in Tanks	Average Albuminoid Ammonia in Effluent, in Grains to Gallons.	Percentage of Purification.	Average Oxygen required for Four Hours for Effluent, in Grains to Gallons.	Percentage of Purification.	Cost of Chemicals including Removal of Sludge, per Million Gallons.
			Tons.	Tons.	Toos. Cwt.	Per cent					£ s. d.
(1) 179 (lime and alumina).	2.019	Lime, 8 cwt.; alumina sulphate, 9 cwt. 22 lb.	4,454	5,996	33 10	14.5	0.245	25	1.9	34	2 13 6
(2) 169 (lime and alumina).	0.506	Lime, 7 cwt. 3 qrs.; alumina sulphate, 10 cwt. 2 qrs.	3,028	2,830	16 14	9.3	0.245	31	1.7	34	1 18 8
(3) 167 (alumina alone).	0.278	Sulphate of alumina, 18 cwt. 1 qr.	4,923	2,223	13 6	4.5	0.220	33	2.1	32	2 11 0
(4) 166 (lime and iron sulphate)	0.793	Lime, 7 cwt. 1 qr.; iron sulphate, 14 cwt.	4,927	2,857	17 3	5.8	0.280	9	2.3	32	2 0 6
(5) 186 (iron and lime).	...	Perchloride of iron, 1 ton; lime, 6 cwt.	3,472	3,298	18 13	9.5	0.250	26	2.2	24	3 2 6
(6) 7½ (electrical).	..	Nil—Electrical	120	71	9 15	5.9	0.168	39	2.1	33	3 0 0
(7) 6 (iron persulphate).	..	Persulphate of iron, 1 ton.	106	51	17 13	4.8	0.160	48	1.6	44	3 7 0
(8) 150 (chloride of lime).	1.197	Chloride of lime, 1 cwt.	1,120	1,478	9 17	13.2	0.422	Nil	3.6	Nil	0 18 0
(9) 162 (lime).	0.740	Lime, 20 cwt.	4,211	3,537	21 15	8.4	0.278	30	2.1	34	1 15 0
(10) 168 (lime).	1.006	Lime, 17 cwt.	4,742	3,983	23 11	8.4	0.266	22	2.9	23	1 14 10
(11) 160 (lime).	0.918	Lime, 15 cwt. 2 qrs.	3,965	3,885	24 9	9.8	0.325	7	1.8	22	1 14 9
(12) 179 (lime).	0.722	Lime, 13 cwt. 2 qrs.	3,882	3,960	22 3	10.2	0.303	5	2.9	3	1 11 0
(13) 173 (lime).	1.601	Lime, 12 cwt. 2 qrs.	3,404	3,812	22 2	11.2	0.315	8	2.4	7	1 10 4
(14) 150 (lime).	0.517	Lime, 18 cwt.	4,080	3,182	..	7.8	0.248	25	2.2	26	1 1 0

Analyses of Sludge dried at 212° F.

	Alumina.	Ferrous Sulphate.	Lime.
Silica . . .	20.93	17.91	13.37
Oxide of iron .	1.83	6.90	1.88
Alumina . .	9.72	8.79	6.93
Copper . . .	0.05	...	...
Lime . . .	14.10	11.18	25.3
Magnesia . .	0.20	0.86	1.74
Phosphoric acid .	0.50	0.92	0.26
Nitrogen . .	0.94	1.35	1.37

	Bleaching Powder.	Electrical.	Ferric Chloride.
Silica . . .	23.3	30.95	15.83
Oxide of iron .	6.42	47.80	5.84
Alumina . .	2.50	...	7.12
Copper . . .	...	...	...
Lime . . .	10.39	...	15.61
Magnesia . .	0.20	...	1.56
Phosphoric acid .	1.75	...	0.74
Nitrogen . .	1.10	...	1.25

The drawback to all precipitation processes is the uncertainty attending them. For some days you may have a good effluent, and then other days bad. The above table clearly proves that to obtain good results from lime not less than from 20 to 25 cwt. should be used, and that in the state of lime-water.

Much better results could have been obtained than those shown in the above table if larger quantities of chemicals had been employed; this is well shown by the following series of experiments:—

Sulphate Alumina to Million Gallons.	Albuminoid Ammonia.	Percentage Purification.	Oxygen for 4 hours.	Percentage Purification.
	Grs. per gall.		Grs. per gall.	
5 cwt. . . .	0.399	10.3	4.0	2.4
10 „ .	0.266	40.2	3.8	7.3
15 „ . .	0.250	43.8	3.6	12.1
20 „ . . .	0.238	46.5	2.8	31.7
30 „ . . .	0.105	76.4	1.0	75.6
40 „ . .	0.100	77.5	0.94	77.0

Sulphate of alumina was added in the proportion of 5 up to 40 cwt. per million gallons of sewage, and it will be noticed how sensibly the percentage of purification rises.

The following experiments were performed to prove that lime was as good a purifier of sewage as sulphate of iron and lime.

The sulphate of iron effluent was made at the sewage works by using millions of gallons of sewage and adding iron sulphate 15 cwt., lime 5 cwt., to the million gallons. The lime effluent was made in the laboratory by adding lime-water to the same sewage at the rate of one ton of lime to the million gallons.

Albuminoid Ammonia in Grains per Gallon.		Percentage Purification.	
Sulphate of Iron Effluent.	Lime Effluent.	Sulphate of Iron Effluent.	Lime Effluent.
0.40	0.24	16	50
0.40	0.24	37	62
0.40	0.38	16	20
0.36	0.24	42	62
0.40	0.20	35	67
0.44	0.36	31	43
0.36	0.28	23	41
0.52	0.32	7	43
0.36	0.20	35	64
0.40	0.20	28	64
0.64	0.32	20	60
0.40	0.24	16	50

This gives an average albuminoid ammonia of 0.42 for iron, and 0.26 for lime, the average percentage purification being for iron 25, and for lime 52. The amount of precipitate caused by lime in the settled sewage is shown in the table annexed.

There is a fair uniformity in the figures given, and taking the average of the twelve experiments there are 21 grains of organic matter precipitated from solution. The alkalinity of the ignited or calcined precipitate is remarkably uniform. This alkalinity is not solely due to lime, as there were only 16 grains of lime added to the gallon, which is about equal to a ton to the million, and as the effluent always contained from 3 to 4 grains of free lime, which, together with the above, makes considerably over 20 grains calculated as lime.

During the last eight years I have experimented with about twenty-five different processes which have been tried at the Salford Sewage Works, and it was only the combination of a precipitating process with that of filtration which produced satisfactory effluents. Even these filtration processes varied in percentage of purification from 50 to 90 per cent. calculated upon the settled sewage. I wish it to be clearly understood that in all my sewage experiments, my purification numbers are upon the settled sewage, except otherwise stated. In my opinion this is the only true method of judging the merits of any process, and it is most fallacious to quote from the shaken sewage. For instance, a shaken sewage might require 6.0 grains of oxygen to the gallon, and the effluent after some patent treatment would require 2.0 grains. It would then be said that there was 66 per

cent. of purification, when in reality there had been none, for when the clear sewage was examined it would be found that it only required 2.0 grains of oxygen to the gallon, the same as the effluent, and the albuminoid ammonia numbers would be found to correspond.

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